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SPECTROGRAPHIC DETERMINATION OF HAFNIUM AND ZIRCONIUM

E. V. Gusyatskaya and A. K. Rusanov

The All-Union Institute of Mineral Raw Materials, Moscow

In developing a method for hafnium determination, we had in mind the analysis of zirconium minerals, ores, and intermediate technical products, by means of quartz spectrographs with average dispersion, which are widely used in factory laboratories, and in geological prospecting work.

The method developed should, in addition, require minimal expenditure of valuable hafnium compounds, so that a technique had to be worked out to ensure freedom from losses of hafnium, and also permit work on small samples. At the same time the possibility had to be borne in mind of extending the method to analysis of other valuable rare elements (Sc, Nb, Ta, rare-earths, etc.).

In developing such a spectrographic method it was not possible to make use of observations made by other authors [1-7], since the work undertaken was a first attempt at adopting quantitative spectrographic analysis instead of X-ray spectrographic analysis for hafnium determination. The methods developed have been used for many years for the determination of hafnium over a wide concentration range of the latter in test materials.

I. ARC ANALYSIS

1. Preparation of Standards and the Technique Used for Taking Spectra

Preparation of standard powders was complicated by the fact that the hafnium dioxide available contained zirconium, the lines of which were clearly discernible on the spectra from both arc and spark discharges. All the available samples of zirconium dioxide and its salts were also, in turn, not free from hafnium.

In order to determine the hafnium content of the zirconium dioxide, and the zirconium content of the hafnium dioxide, in addition to X-ray spectrographic analysis, another method was used which was based on analysis of the shape of the curve relating the relative intensities of the hafnium and zirconium lines to the concentrations of these elements in standard powders of the oxides.

To prepare standard powders of the isomorphous compounds of the oxides of hafnium and zirconium, aliquots of the zirconium and hafnium dioxides, respectively, were fused in porcelain crucibles with potassium bisulfate, the melt dissolved in 1% sulfuric acid and the solutions obtained made up to standard volumes. By mixing various amounts of the respective hafnium and zirconium solutions, a number of standards were prepared with known ratios of hafnium and zirconium. Hafnium and zirconium were precipitated from the solutions as hydrated oxides by means of ammonia; the precipitates were filtered off, dried, and calcined to zirconium and hafnium dioxides.

By mixing these basic standards with corresponding amounts of the oxides of various elements it was possible to obtain powders approximating in composition to zirconium ores and minerals.

For arc analysis, the zirconium and hafnium dioxides, as well as natural minerals and mixtures of the various elements oxides corresponding in composition to the minerals, were placed in 5 mg lots in the canal of the lower positive electrode with a diameter of 5 mm. The depth of the opening had to be not less than 4 mm, otherwise the infusible powder of the zirconium and hafnium compounds in the first few moments after the arc had been switched on, was ejected from the opening by the air stream. The diameter of the opening was 2 mm.

A two fold magnified image of the voltage arc was projected by a quartz lens on the spectrograph screen fixed between the lens and the spectrograph slit; the screen had a 4 mm opening for transmitting the light from the central part of the arc flame. The distance between the electrode tips during arcing was 4 mm. The arc was supplied with a 9 ampere D.C. current from a mercury rectifier operating at 240 V. The spectra from 2500-3500 A was photographed on a ISP-22 spectrograph, and on a Hilger Auto-Collimating quartz spectrograph.

2. Effect of Fractional Distillation of the Elements on Line Intensity

Evaporation of ores and minerals in a carbon arc is usually accompanied by fractional distillation of the melt, during which the most volatile compounds of the elements pass into the arc flame first.

The general sequence in which the elements pass into the arc flame from melts has been established previously [8]. In the case of zirconium minerals, however, the order in which the elements pass into the arc have only been studied on three minerals: zirconium, baddeleyite, and eudiolite. It was, therefore, of decisive interest to determine the sequence in which these elements pass into the arc flame from other zirconium minerals. Fractional distillation of the elements was also investigated from mixtures of the element oxides in which the molar ratios of ZrO_2 to other oxides were 1:1, 4:1, 1:4.

In order to study these fractional distillations of the components of various zirconium minerals into the carbon arc, the spectra of the arc flame were photographed on a photographic plate moving at a uniform speed.

The information obtained on changes in line intensity during evaporation of the elements, show that the picture of the way in which the elements pass into the flame does not change essentially for a wide range of molar ratios. An idea of the sequence in which the lines appear in the spectra, and how their line intensities change during evaporation of a few zirconium minerals may be gained by examination of Figs. 1-7. Fig. 8 represents a picture of the mutual positions of the most characteristic lines of the elements on a spectrogram in the form in which they are usually observed on examining photographs under a spectro-projector. In all cases, the most volatile components of the metls pass into the arc flame first; arsenic, zinc, cadmium, bismuth, antimony, sodium, potassium, boron, and lead.

Zirconium and hafnium pass into the flame at the same time as thorium, niobium, tantalum and the rare-earths, after complete evaporation of the volatile components. Titanium also passes into the arc flame after removal of the readily volatile components but, nevertheless, evaporates a little earlier than zirconium and hafnium. This shows up especially clearly for melts with large zirconium and hafnium contents.

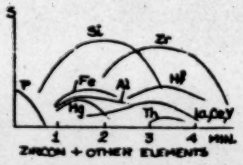
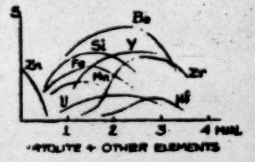


Fig. 1

Fig. 2



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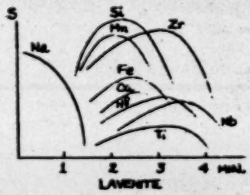

Fig. 4

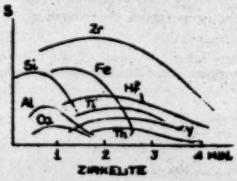

Fig. 5

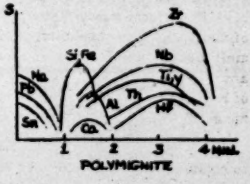

Fig. 6

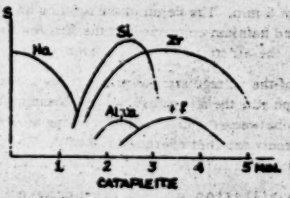

Fig. 7

Figs. 1-7. Changes in line blackening during evaporation of minerals in the carbon arc.

Iron, cobalt, nickel, silicon, and vanadium follow after evaporation of the readily volatile components, but appear in the flame before zirconium and hafnium. Evaporation of these elements also finishes sooner than that of hafnium and zirconium. Manganese, magnesium, chromium and copper start to appear at the same time as iron, cobalt, nickel, vanadium and titanium, but evaporate more rapidly than these elements. Calcium resembles the rare-earths in its behavior, but it is slightly more volatile. Molybdenum and tungsten, which form readily volatile oxides, start to pass into the flame with the volatile components of the melts. The presence of molybdenum and tungsten in the arc flame can, however, be detected at the moment when zirconium and hafnium evaporate. Hafnium and zirconium evaporate at the same time in all cases.

Fig. 8. Change in blackening of the lines of the elements on spectrograms during evaporation of mixtures of the oxides of zirconium and other elements in the ratio 1:1.

These experiments, the sequence with which the test elements pass into the arc flame, and the length of time for which their lines appear during evaporation of zirconium minerals and melts of the oxides, permit these elements to be arranged in the following order:

As, Cd, Zn, Bi, Pb, Sb, Na, B, Sn, Mo, W, Mn, Mg, Cu, Fe, Co, Ni, Si, V, Cr, Al, Be, Ca, Ti, rare earths, U, Th, Nb, Ta, Hf, Zr

This series is, in most respects, similar to the volatility series of the elements compiled previously [8].

This fractional evaporation of the elements into the arc flame complicates analysis and must have primary consideration when studying zirconium ores and minerals, the composition of which may differ appreciably in the number and amounts of the respective elements.

As indicated already, with respect to passing into the arc flame, the closest in their behavior are hafnium and zirconium, whose lines appear and disappear at the same time, independently of the composition of the zirconium ores and minerals tested.

Thus, measurements of the relative intensity of the hafnium and zirconium lines in the spectra of zirconium ores and minerals, can give valuable information about hafnium-zirconium ratios in the test samples. One must bear in mind, however, that fractional evaporation of the ores may lead to changes in composition of the gas cloud in the arc, and, consequently, to a change in the temperature of the latter, which in its turn, affects line intensity. As was shown experimentally, during evaporation of zirconium ores and minerals, there is a continuous, sometimes, step-like increase in arc flame temperature, which attains a value of 7400° for complete evaporation of test material.

As an example, we have adduced in Fig. 9 the change in temperature of the arc flame during evaporation of a zircon in a carbon arc supplied with a 5 ampere D.C. current. The arc distance was maintained constant at 4 mm in this instance. Fig. 9 also illustrates the passage of silicon and zirconium into the arc flame. The continuous increase in temperature of the arc flame during evaporation of a zircon, is also confirmed by changes in the difference in blackening of the spark and arc lines of Hf II 2808.0 and Hf I 2866.4, the relative intensity of which increases with increased flame temperature.

The normal methods used for stabilizing arc temperature, by adding compounds of elements with low ionization potentials, do not lead to satisfactory results when investigating the composition of zirconium ores, since the elements added do not normally pass into the flame at the same time as the only slightly volatile oxides of zirconium and hafnium. Direct introduction of compounds of elements with low ionization potentials into the arc flame on a wick does not give positive results either, during analysis of zirconium ores, since in this case the spectra of hafnium and zirconium are seriously weakened.

What has been said above leads one to conclude that a reasonably accurate determination of hafnium and

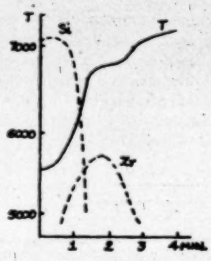

Fig. 9. Change in arc flame temperature during evaporation of a zircon ($ZrSO_4$); evaporation curve for silicon and zirconium.

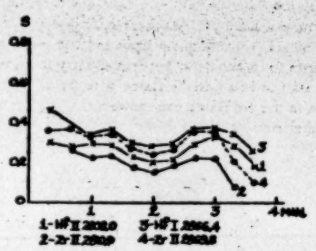

Fig. 10. Relation between line blackening of zirconium and hafnium on length of evaporation of a mixture of 56% HfO_2 and 44% ZrO_2 in a carbon arc.

zirconium in ores and minerals, on the basis of measurements of the relative intensities of the lines of these elements does not seem to be an easy matter.

Analysis of zircons by using standard mixtures of the dioxides of zirconium, hafnium and silicon confirmed that it is possible to determine the ratio of hafnium to zirconium in these minerals, but at the same time it also showed that considerable deviations may occur between duplicate determinations in a number of instances.

It should be noted that the use of the standard mixtures indicated for determination of hafnium-zirconium ratios, may lead to systematic errors when analyzing other minerals.

Determination of hafnium in zirconium dioxide is another matter, since the evaporation of the latter is not accompanied by fractional distillation of other elements into the arc flame. Moreover, for the analysis of zirconium dioxide it is possible to use a spark discharge for exciting the spectrum, and this ensures a fairly high accuracy for hafnium determination. For spectrographic analysis of zirconium minerals and ores it is, therefore, more expedient to subject the samples to preliminary chemical treatment to convert them into zirconium and hafnium dioxides. Chemical methods of isolating the dioxides of zirconium and hafnium from ores have been worked out to a sufficient extent at present to enable this operation to be carried out without much difficulty.

3. Determination of Hafnium in Zirconium Dioxide

When a melt of the dioxides of zirconium and hafnium are evaporated in a carbon arc, in contrast to zirconium ores and minerals, no fractional distillation of the elements which complicate quantitative determination of hafnium and zirconium occurs. These elements pass at a more uniform rate into the arc flame, and as can be seen from Fig. 10, during the evaporation process, there are no sudden changes in line intensity which are characteristic of the spectra of zirconium ores and minerals. The decrease in line intensity during the second minute

Fig. 11. Relation between difference in blackening of hafnium and zirconium lines on the length of evaporation of a mixture of 56% HfO_2 and 44% ZrO_2 in a carbon arc.

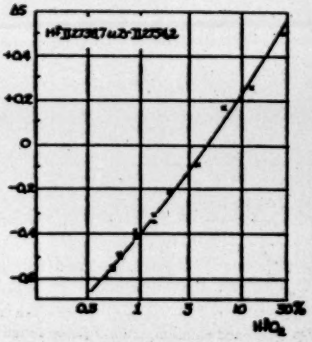

Fig. 12. Relation between difference in blackening of the Hf II 2738.7 and Zr II 2758.2 lines and the hafnium content of the zirconium dioxide.

of arcing is of a random nature, and is determined by temporary removal of the arc flame from the evaporating dioxides as a result of irregular burning on the edges of the carbon electrode.

From Fig. 11 it is clear that on switching from absolute values of the blackening to differences in their blackening, the curves are practically parallel to the abscissa during the evaporation time indicated. It is noteworthy that the curves behave similarly for the pair of lines made up of the spark and arc lines of hafnium, the relative intensity of which is particularly dependent on the temperature of the arc flame. This indicates that during evaporation of zirconium and hafnium dioxides there is no significant change in arc flame temperature. Measurement of the potential difference across the carbon electrodes of the burning arc showed that the flame temperature remains at a level of ca. 7000° almost through the whole extent of the evaporation of hafnium and zirconium dioxides; this gives rise to favorable conditions for the quantitative determination of these elements with an error of $\pm$ 8-10% for a single determination.

Determination of the hafnium and zirconium dioxides content was made by means of calibration curves, in which the logarithm of the concentration of the hafnium dioxide, or zirconium dioxide, was plotted on the abscissa, while the corresponding values of the difference in blackening between the lines of hafnium and zirconium were plotted along the ordinate. The calibration curve used for the determination of hafnium in zirconium dioxide is given in Fig. 12 as an example. Table 1 lists the analytical pairs of lines used, as well as the concentration ranges of hafnium and zirconium dioxides determined by means of them.

TABLE 1

Wave length in A		Concentration range (%)	
hafnium	zirconium	HfO_2 in ZrO_2	ZrO_2 in HfO_2
II 2738.7	II 2754.2	0.1-55	–
II 2622.7	II 2630.9	0.1-55	–
II 2738.7	II 2742.55	–	0.1-65

It is noteworthy that the concentration ranges given in Table 1 for low contents of hafnium and zirconium are not limiting, and are determined exclusively by the amount of one of the elements in the dioxides used for making up standards. Extrapolation of the calibration curves obtained by plotting log C and log I_{Hf}/I_{Zr} (the background correction being taken into account) shows that it is possible to determine hundredths of a percent of hafnium in zirconium dioxide, and of zirconium in hafnium dioxide. This hypothesis has been confirmed subsequently by N. F. Zakhariya and S. M. Solodovnik using the lines Hf II 2641.4 and Zr II 2619.2.

For rapid, orientating, determinations of hafnium in zirconium in oxide powders a method can be used which is based on visual determination of the equality of blackening of the lines of the elements in the spectrum of the test sample. The multilinearity of the spectra which normally complicates determination of hafnium and zirconium, in the given instance, favors the selection of a considerable number of analytical pairs of lines for a wide concentration range of the dioxides of hafnium and zirconium in test powders. These pairs of lines can be conveniently found from an atlas of photographs of arc spectra of zirconium for the region 2500-3500 A, in which the position of the analytical lines of hafnium and zirconium are given graphically, and in which it is indicated at what HfO_2 content, these lines have equal blackening.

II. SPARK ANALYSIS

1. Preparation of Standard Electrodes and the Technique of Photographing the Spectra

Completely satisfactory conditions for the excitation of the spectra of hafnium and zirconium which ensure the necessary accuracy for determining these elements, can be achieved by using a spark discharge between metallic electrodes, in which the hafnium and zirconium oxides are evenly distributed. The latter condition can be easily fulfilled by preparing compressed electrodes from mixtures of metal powders and the dioxides of hafnium and zirconium. The method of preparing an isomorphous mixture of ZrO_2 and HfO_2 with known ratios of these elements has been described earlier.*

Most satisfactory results were obtained by using silver, which does not change during spark discharges. The surface of the silver tablets during a spark discharge was only covered with a characteristic iridescence which indicates formation of a very thin film of oxide.

Powdered silver was made by gradual addition of powdered zinc to a slightly acid sulfuric acid solution of silver nitrate. The spongy metallic silver, which separated out, was treated with 5% sulfuric acid in order to free the silver from possible contamination with zinc. When no more bubbles of hydrogen were evolved, the spongy mass was

* N. F. Zakhariya showed later that is possible to use a mechanical mixture of ZrO_2 and HfO_2.

washed first with distilled water, and then with alcohol, and finally squeezed between sheets of filter paper, and dried in an oven. The powdered silver prepared in this way was finally sieved through a 0.3 mm mesh sieve.

The mixture of powders consisting of 75% silver and 25% metal oxides after careful grinding in an agate mortar was pressed in a steel press former into moldings with a diameter of 4 mm. The required pressure of 2000 kg/cm^2 is easily attained with a hand oil press. In order to increase the stability of the electrodes they were calcined for a short time in air at ca. 800°. In contrast to electrodes which have not been calcined, the surface of calcined electrodes is so stable that they can be worked with a file and do not break up during spark discharge.

Since we did not have a large amount of hafnium dioxide at our disposal, electroder in which the content of the latter was high were made only 1-1.5 mm in length. This gave rise to the danger of forming a spark discharge between the electrode holders, and to the appearance of the spectra of the latter. In order to get longer electrodes, therefore, after filling the press former with the requisite mixture of silver powder and hafnium dioxide, pure silver powder was added. By this method a pellet of pure silver was obtained with only its tip consisting of a mixture of silver and the dioxides of zirconium and hafnium.

Such a technique of preparing the electrodes ensures, where necessary, getting electrodes for which only a few milligramsof hafnium and zirconium are necessary. This method opens up the possibility of using a spark discharge for getting spectra of other non-conducting valuable materials such as the oxides of the rare-earths, tantalum, niobium, scandium, etc..

Graphite can be used instead of silver. The tablets obtained in these cases, however, do not have that stability which is characteristic of tablets made from silver.

A Feisner spark exciter was used to get the spectra.(Transformer voltage 8,000, capacity 0.003 μF, self inductance 800,000 cm.) Similar results were obtained when the IG-2 spark generator was used.

The spark was formed between one of the pressed electrodes fitted in a vertical position and a conical, spectroscopically pure graphite rod with an area of 3 mm diameter at its tip. The interelectrode distance, which was 3 mm, was checked with a glass gauge. The electrode holder was a spectroscopically pure graphite cylinder 5 mm in diameter; an opening 1.5 mm in depth was drilled in its upper end, and the lower end of the electrode made,from pure silver, stuck into it.

When the spark discharge is passed,the surface of the pressed electrode is subjected uniformly to the same treatment, so that there is no break-down of the latter.

The upper electrode and the graphite holder should, after taking the spectra, be carefully wiped, or better still, should be replaced by new ones, since the discharge is accompanied by spraying of the silver electrode, and by the formation of a scarcely observable coating of silver and oxides of zirconium and hafnium on the top end of the electrode, and also on the tip of the graphite holder.

The ISP-22 spectrograph fitted with a triple lens illuminating system was used for photographing the spectra. The exposure time for photographing the spectra on plates with a sensitivity of 250 H and D was 40 seconds.

A set of standard electrodes,prepared as described above, can be used for a very long time, since the amount of electrode material consumed per photograph does not exceed 0.1 mg; this corresponds to an expenditure of ca. 0.02 mg of a mixture of hafnium and zirconium oxides. Thus, one standard electrode, which has been made from ca. 5 mg of a mixture of zirconium and hafnium oxides, can be used for taking several hundred spectra photographs.

2. Determination of Hafnium in Zirconium Dioxide and of Zirconium in Hafnium Dioxide

Calculation of the percentage of hafnium and zirconium in test samples of the oxides is made by means of calibration curves expressing the relation between the difference in blackening of the hafnium and zirconium lines, and their percentages in the sample of dioxides. The calibration curves were obtained by using a set of standard electrodes, the spectra of which were photographed on a photographic plate at the same time as the spectra of the electrodes made from the test dioxide mixtures.

As an example we have adduced in Fig. 13 a calibration curve for the lines Hf II 2641.4—Zr II 2643.4, which covers low concentrations of hafnium in zirconium dioxide. For the construction of calibration curves within the coordinates — logarithm of the relative intensity of the lines and log of the concentration — the curve constructed previously may be used.

The concentration ranges, in which hafnium and zirconium can be determined, the wave lengths of the pairs of lines photometrically measured, and the errors of one single determination for each pair of lines are given in Table 2.

TABLE 2

Wave lengths in A		Element determined	Concentration range (%)	Accuracy of determination (cf. probable error) (%)
zirconium	hafnium			
II 2643.4	II 2641.4	hafnium	0.5-82	± 5
II 2550.7	II 2551.4	hafnium	0.5-82	± 5
II 2643.4	II 2641.4	zirconium	0.5-85	± 5
II 2550.7	II 2551.4	zirconium	6-75	± 6

The calibration curves for the selected pairs of lines can be continued up to a content of 0.1% of HfO_2 and ZrO_2 in the respective dioxides, if the curves are plotted using as coordinates — logarithm of the relative intensity of the lines and logarithm of the concentration of the test element, a correction being applied for background near the lines.

The presence of other contaminating elements in the dioxides of zirconium and hafnium usually has little effect on the analytical results. Thus 10% iron does not change the relative intensity of the hafnium and zirconium lines (Fig. 14). Consideration of Fig. 15 shows that normal changes in the value of the spark distance does not lead to appreciable errors in the analysis of zirconium and hafnium dioxides.

Possible changes in the ratio of silver to test oxide powder in the electrode, just as changes in the pressure used for making the electrodes, do not give rise to any significant errors in the spectrographic determination of hafnium and zirconium (Figs. 16 and 17).

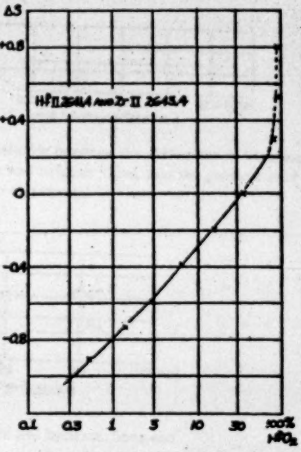

Fig. 13. Relation between differences in blackening of the lines Hf II 2641.4 and Zr II 2643.4 and the amount of hafnium in the zirconium dioxide.

A very positive factor in the analysis of the oxides of hafnium and zirconium is that the continued effect of arcing on the electrode surfaces does not lead to any appreciable change in the relative intensities of the hafnium and zirconium lines (Fig. 18). The absence of any relation between the analytical results and duration of arcing, as well as the small amount of electrode used up in a test is of great practical importance, since it permits standard electrodes to be used for a long time and to get several hundred spectra photographs for each of them.

Fig. 14. Effect of ferric oxide on the difference in blackening between the lines of zirconium and hafnium.

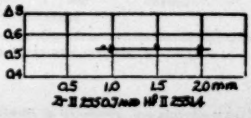

Fig. 15. Effect of the spark gap on the difference in blackening between the lines of zirconium and hafnium.

It is noteworthy that during sparking there is no preferential evaporation of silver, and, consequently, enrichment of the surface with oxides of zirconium and hafnium which have a very high boiling point, e.g., the relative intensity of the silver and zirconium lines, and of the silver and hafnium lines, respectively, depend only to a small extent on the length of time for which the spark is operating. This indicates that the composition of the surface layer of the electrodes is constant before and after the spark discharge. As an example, Fig. 19 illustrates the change in difference in blackening of the silver and zirconium lines at various times during the spark discharge.

It is of interest to note that when the electrodes are sparked for a long time, there is no regular change in the differences in blackening of the pair of lines consisting of the arc line of silver and the spark line of zirconium, while the scatter of points for this pair does not differ from the scatter of points for the more homologous pair of lines consisting of the spark lines of silver and zirconium. This shows that the excitation conditions in the spark depend only to a small extent on the time during which the surface of the electrode is subject to the spark discharge.

Fig. 16. Relation between the difference in blackening of the zirconium and hafnium lines and the silver content of the electrode.

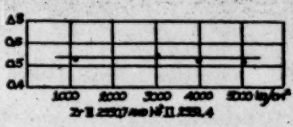

Fig. 17. Relation between the difference in blackening of the zinc and hafnium lines, and the pressure used for making the electrodes.

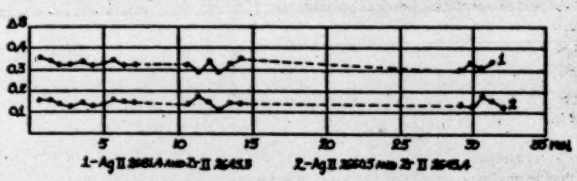

Fig. 18. Relation between the blackening of the zirconium and hafnium lines and the time of operation of the spark discharge.

The insignificant dependence of the relative intensity of the silver and zirconium lines, on the length of time for which the spark is operated, indicates that it is possible to determine hafnium and zirconium by means of the difference in blackening of the lines of these elements, and the silver line on the spectrograms. The scatter of

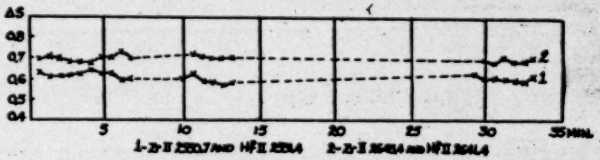

Fig. 19. Relation between differences in blackening of the silver and zirconium lines and the time of operation of the spark discharge.

points on the calibration curves for the pair of lines silver-hafnium (zirconium) is, however, greater than for curves drawn up on the basis of the differences in blackening of the zirconium and hafnium lines.

It should be remembered that the experimental errors of determinations based on the use of hafnium and zirconium lines, are, in the main, determined by errors in photography and in photometric measurements of the spectra, amounting to ± 4%. This indicates that the accuracy of determination based on the use of the analytical pairs of lines hafnium-zirconium already achieved is not limiting, and can be increased by using better quality photographic paper. Experimental accuracy can also be increased by taking several photographs and averaging the results.

SUMMARY

1. Arc and spark methods have been worked out for quantitative determination of hafnium, which are designed for use in prospecting for hafnium raw materials and for the control of hafnium extraction processes, they are suitable for use under laboratory and factory conditions in which spectrographs of average dispersion are used.

2. Using the dioxides of hafnium and zirconium as examples, a spark method has been worked out for the analysis of small amounts of the non-conducting compounds of these valuable elements, whereby several spectra can be taken with very small expenditure of test material.

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EFFECT OF THE STRUCTURE OF THE OXIME MOLECULE ON THE PROPERTIES OF ITS COMPOUNDS WITH METALS

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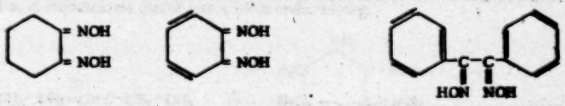
L. A. Chugaev [1] was the first to study the series of compounds formed by α-dioximes with metals and to show that these compounds differ in color, and in behavior toward solvents.

Systematic study of the properties of a series of compounds formed between metals and oximes permits one to establish a relation between the molecular structure of the metal oxime and the properties of this compound.

Modern research shows that it is completely inadequate to consider the "value" of an organic reagent purely from the viewpoint of the presence in the given molecule of a characteristic group of atoms. This is clearly illustrated in the compounds of the following oximes, 1,2-cyclohexanedionedioxime, benzophenonedioxime, and α-benzyldioxime.

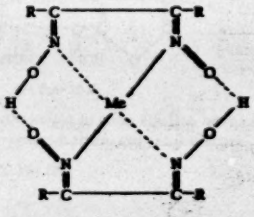


(1) (2) (3)

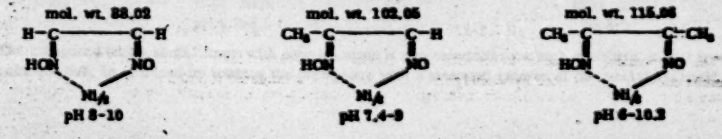
Benzophenonedioxime (2) gives characteristic compounds; in the case of α-benzyldioxime (3), in which the carbons do not form part of the ring, the capacity of the dioxime to give inner complex compounds of the type given by 1,2-cyclohexanedionedioxime is reduced. We shall consider the effect of the structure of the dioxime on the properties of its compounds with metals in the following examples.

The Relation Between the Structure of Nickel Dioximes and the pH Range at which They Are Formed

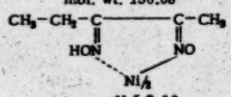
By a systematic investigation of the compounds formed between dioximes and metals, in the first instance with nickel, we ascertained that the compounds formed between nickel and various dioximes at various pH's maintain the same structure:



If we consider from this point of view the compounds formed between nickel and a series of aliphatic α-dioximes, starting with the simplest glyoxime, and gradually introducing CH_3 groups, then we can follow a systematic change in the pH value of the solution at which the corresponding nickel derivative is formed.



mol. wt. 130.08



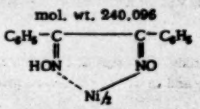
pH 5.2-10

mol. wt. 144.096

pH 5-10.5

We observe that with increasing chain length, the nickel compound is formed at lower pH values, which indicates a high mobility for the hydrogen of the salt-forming oxime group. The benzene ring in α-benzyldioxime has a similar effect:

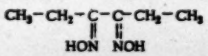
mol. wt. 240.096



pH 4.2-11

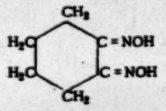
Of all the compounds formed between nickel and α-dioximes the most stable in both acid and alkali media is its compound with 1,2-cyclohexanedionedioxime. This dioxime is the most valuable reagent for gravimetric determination of nickel.

The effect of the cyclic group on the structure of the reagent itself is clearly demonstrated in this compound. 1,2-Cyclohexanedionedioxime and diethyldioxime have an equal number of carbon atoms; 1,2-cyclohexanedionedioxime can be regarded as diethyldioxime closed into a six-membered ring.



Diethyldioxime

mol. wt. 144.096

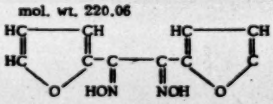


1,2-Cyclohexanedionedioxime

mol. wt. 142.08

These reagents differ strongly in their reactions with metals. The possibility of forming compounds with metals (Ni, Fe, Pd) in more acid media, the high stability of the nickel derivatives in alkali and ammoniacal solution are among the advantages possessed by cyclohexanedionedioxime. It is of interest to note, that α-furildioxime, which has conjugated bonds and oxygen in the heterocycle, gives a compound with nickel in more alkaline media (pH 6.4-10.5); here probably there is a resemblance between the hydrogen of the salt-forming NOH group and the oxygen of the heterocycle

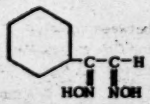
mol. wt. 220.06



pH 6.4-10.5

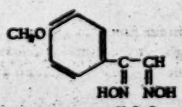
The formation of compounds with nickel in more alkaline media is also characteristic of the reaction of nickel with the unsymmetrical dioximes, α-phenyldioxime and anisyldioxime

mol. wt. 164.08



pH 6.2-8.5

mol. wt. 195.09

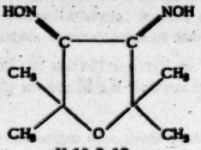


pH 8-9

The compound which nickel forms with anisyldioxime is characterized by a high solubility, so that quantitative results can only be obtained by washing the precipitate with a saturated solution of the precipitate itself.

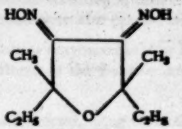
The compounds formed between nickel and the dioximes of tetramethyl-, and dimethyldiethyltetrahydrofuran are formed in much more alkaline media

mol. wt. 187.11



pH 10.2-12

mol. wt. 214.14



pH 10-12

The upper limit pH (ca. 12) was only determined roughly since these dioximes were studied from the point of view of their use in colorimetric determinations.

In comparing the properties of the various nickel oximes it is of interest to note that they do not depend on the molecular weight of the dioxime, but on its solubility in water.

The most valuable reagent for the gravimetric determination of nickel is 1,2-Cyclohexanedionedioxime. This dioxime has a fairly low molecular weight (M = 142.08), and is readily soluble in water. Consequently, the molecular weight and the solubility of the reagent itself are not the decisive factors in selecting the most valuable reagent from an analytical point of view.

α-Benzyldioxime, which has a considerably higher molecular weight (240.09) also forms a compound with nickel in fairly acid media (pH ca. 4), but its particularly low solubility lowers its values as a reagent in comparison with 1,2-cyclohexanedionedioxime.

The case of 1,2-cyclohexanedionedioxime illustrates that there is no connection between the solubility of the reagent itself in water and the solubility of its compound with nickel. It should be noted, however, that in the case of a series of symmetrical aliphatic dioximes and of α-benzyldioxime there is a relation between solubility of the metal dioximes and the molecular weight of the reagent with increasing molecular weight; the solubility of the nickel compound decreases, since the latter depends on the pH range at which the nickel derivative is precipitated. For unsymmetrical dioximes having hydrogen instead of one of the radicals, there is a common property — their nickel compounds have a large tendency to dissolve in alkalis. This is especially apparent with metallic derivatives of dioximes with aromatic radicals (phenyl- and anisyldioximes).

TABLE 1

Formation of Compounds of Ni and Pd According to the Acidity of the Solution

Reagent	Element	Acidity
Dimethylglyoxime	Pd	2N HCl
	Ni	pH 5.5
1,2-Cyclohexane-dionedioxime	Pd	5N HCl
	Ni	pH 3.2-3.4

TABLE 2

Distribution Coefficients and Values of ε for Certain Nickel Dioximes

Dioximes	ε λ 427	Distribution coefficient
α-Nickel furildioxime	10,000	47
Nickel methylethyldioxime	1,700	55
Nickel phenyldioxime	4,600	26
Nickel anisyldioxime	8,100	2

The effect of the structure of the reagent molecule can be traced through the mono-oxime compounds. Nickel and cobalt give coordination compounds with acetyl monoximes of the composition $[MeX_2 \cdot 4CH_3CH=NOH]$; formaldioxime forms a compound with a new type of bond

$$[Ni(CH_2=NO)_2]Na_2 \qquad [Co(CH_2=NO)_2]Na_2$$

Molecular structure also affects the capacity of the oxime to combine with metals under varying conditions; this is clearly illustrated by the conditions under which the dioximes of palladium and nickel are precipitated.

Relation Between the Structure of the Dioxime Molecule and Its Chromophoric Action

Let us consider the effect of the molecular structure of the oxime on colorimetric methods. The capacity of metal dioximes to dissolve in non-aqueous solvents to form colored solutions [1, 2], can be used for colorimetric determinations. The value of such a reagent is determined by two factors — the molar extinction coefficient which determines the sensitivity of a colorimetric reaction at a certain wave-length, and the distribution coefficient. The preproducibility of the distribution coefficient characterizes the optimum conditions for carrying out the colorimetric reaction.

Chugaev in his work, in which he considered the properties of metal dioximes, noted the solubility of the inner-complex compounds formed in chloroform or benzene.

We have carried out determinations of the distribution coefficients for a number of nickel dioximes under the conditions used for colorimetric analysis. A more accurate criterion for selecting optimum conditions is the constancy of the percentage extraction; determination of distribution coefficients were also carried out under these conditions.

Dioximes of metals (Ni and Pd) in which the dioxime molecule is unsymmetrical or the dioxime contains a furan radical, are highly soluble in non-aqueous solvents. The polarity of the dioxime molecule obviously affects the extraction process.

Comparative determinations were made of the distribution coefficients, using chloroform as solvent. Table 2 contains results for the distribution coefficients, and the molar extinction coefficients for nickel dioximes which are of great interest in practical colorimetry.

The molar extinction coefficient was calculated for the maximum value of the optical density of the visible part of the spectrum. Nickel α-furildioxime has a maximum on the light absorption curve in the visible part of the spectrum at 436 mμ; the maxima of the other metal dioximes are in the short wave part of the spectrum. Each of the compounds considered possesses some valuable property. The most sensitive reaction is that between nickel and α-furildioxime, as is evident from the value of ε, this reaction is a suitable one to use in practice, since the value of its distribution coefficient is high, thus testifying to a large solubility of the compound in chloroform. Nickel methylethyl dioxime has the highest solubility in chloroform; this is confirmed by its high distribution coefficient. Of the compounds considered, this compound has the least value of ε, but is of great interest nevertheless, since, apart from the fact that it enables nickel to be determined in the presence of other metals which do not react with it, under the conditions used for nickel determination, methylethyl dioxime can also be used, as we showed, to determine nickel in the presence of cobalt.

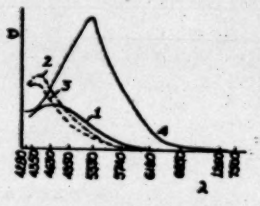


Fig. 1. Absorption spectra of Re with: 1) 1,2-cyclohexanedionedioxime; 2) dimethyldioxime; 3) methyldioxime; 4) α-furildioxime.

The other dioximes are also valuable reagents for the colorimetric determination of nickel, thanks to the high sensitivity of their reactions with nickel. The distribution coefficient of anisyldioxime could obviously be increased by using another solvent instead of chloroform, or by using a mixture of solvents.

TABLE 3

Molar Extinction Coefficients for the Compounds Formed Between Rhenium and Various Dioximes

Dioxime	λ in mμ	ε
Methyldioxime	436	10,000
Dimethylglyoxime	436	11,000
1,2-Cyclohexanedionedioxime	465	5,800
Furildioxime	533	167,000
Furildioxime	−533	24,000 in $CHCl_3$

TABLE 4

Molar Extinction Coefficients of the Compounds $[Fe \cdot 2Py]^{2+}$

Reagent	ε 480–520 mμ
Methyldioxime	5,400
Dimethylglyoxime	6,400
Methylethyldioxime	7,000
1,2-Cyclohexanedionedioxime	9,800

The unsymmetrical dioximes, and α-furildioxime are, therefore, of great interest for colorimetry. The compounds of α-furildioxime with other metals are of particular importance. Thus, the compound formed between α-furildioxime and bismuth has a considerably more intense color than the other dioximes of bismuth. The dioximes of lead are all colorless apart from lead α-furildioxime; the latter has a yellowish color.

α-Furildioxime is related to the unsaturated compounds for which absorption in the longer wave bands is characteristic; as a result the nickel and copper derivatives show maximum light absorption in the visible spectrum.

The effect of the structure of the reagent molecule can also be well-illustrated in the compounds of rhenium with α-dioximes, by comparing their absorption spectra (Fig. 1), in which displacement of the light absorption maximum can be seen. Table 3 lists the absorption coefficients.

The compound formed between rhenium and α-furildioxime can be extracted with chloroform.

The effect of the structure of the reagent is also clearly demonstrated in the case of iron compounds, particularly in their absorption spectra (Fig. 2), and in the molar extinction coefficients (Table 4).

The colors of solutions of bivalent iron with dioximes are considerably more stable in the presence of pyridine. the compounds are extracted by non-aqueous solvents, which is of considerable interest from a practical point of view. The compounds of iron with 1,2-cyclohexanedionedioxime is of special interest, two compounds are formed, one in acid solution (pH 3) and the other in alkaline solution (pH 10).

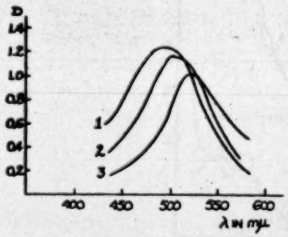
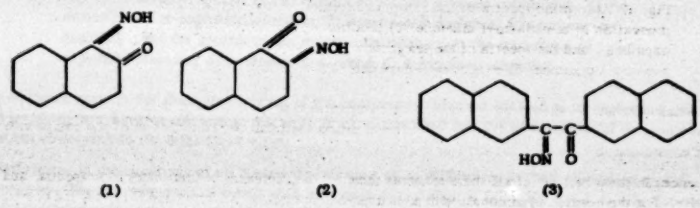


Fig. 2. Absorption spectra of the compounds of Fe with: 1) methylethyl dioxime; 2) dimethyl glyoxime; 3) methyl glyoxime.

It is possible to follow the transition from one compound to the other on the absorption spectra (Fig. 3). The composition of the compound in the presence of ammonia and pyridine corresponds to $Fe:DH_2 = 1:2$ [3]. This reagent is also of interest because it permits work to be carried out in acid media with trivalent iron. The compound of iron with 1,2-cyclohexanedionedioxime can be extracted with non-aqueous solvents. Thus, the dioxime of 1,2-cyclohexanedionedioxime occupies a special position among dioximes as a reagent for iron.

The influence of the structure of the reagent molecule can also be demonstrated by taking the compounds of cobalt as examples. Let us consider, e.g., the compounds of cobalt with α-nitroso-β-naphthol, β-nitroso-α-naphthol, and the monoxime of naphthoyl diketone first synthesized at our request by V. A. Zagorsky and student D. Kuznetsov in the Dept. of Organic Chemistry of Moscow State University.



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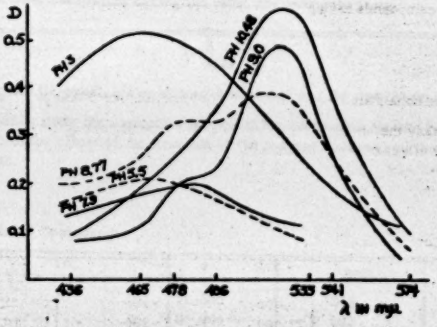

Fig. 3. Effect of pH on the change in the absorption spectra of the compound of iron with cyclohexanedionedioxime.

This work was undertaken to confirm the correctness of our ideas on the structure of the first two reagents as having quinoneoxime groups at the moment of formation of the complex compounds with cobalt [4]; α-nitroso-β-naphthol, and β-nitroso-α-naphthol, are valuable reagents for cobalt (Fig. 4).

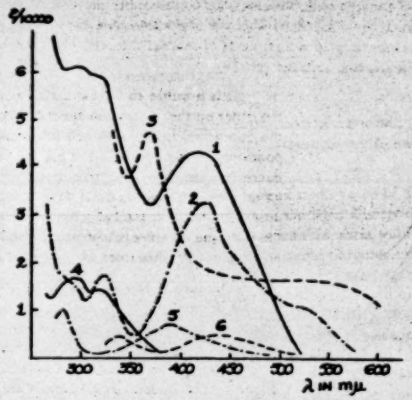

Fig. 4. Absorption spectra of the compound formed between cobalt and: 1) the monoxime of α-naphthoyl diketone; 2) α-nitroso-β-naphthol; 3) β-nitroso-α-naphthol; and the spectra of the reagents themselves; 4) the monoxime of naphthoyl diketone; 5) α-nitroso-β-naphthol; 6) β-nitroso-α-naphthol

Additional work on the absorption spectra of the compounds discussed enabled us to work out a colorimetric method involving non-aqueous solvents; in this work it was established that the composition of the compounds which separate out correspond to the ratio Co : R = 1:3.

Differences in the structures of all these reagents show up as differences in their absorption spectra, and in reaction sensitivity. For the compound of cobalt with α-nitroso-β-naphthol, ε is 32,000 and λ is 418, the corresponding values for β-nitroso-α-naphthol are 48,000 and 360; and for the monoxime of naphthoyl diketone 46,000 and 405. A study of the properties of these compounds having the same characteristic group

showed that the best reagents for cobalt are α-nitroso-β-naphthol and the monoxime of α-naphthoyl diketone.

It is of great interest to study the absorption spectra of the compounds formed between metals and organic reagents in order to confirm the effect of the structure of the reagent molecule on the properties of the compound formed in the ultra-violet.

TABLE 5

Molar Coefficients for Nickel Compounds

Reagent	ε	λ_{max}	ε	λ_{max}
Dimethylglyoxime	16,000	285	1,100	427
α-Furildioxime	27,000	290	10,000	465

We concluded that the structure of the oxime affects the properties of its compounds with metals.

SUMMARY

It has been established that the structure of the oxime molecule affects the mobility of the hydrogen of the salt-forming oxime group, thereby leading to the formation of nickel compounds at varying pH's.

The structure of the oxime determines the value of a reagent for colorimetric reactions for metals, from the point of view of the value of the molar extinction coefficients and the distribution coefficients of the compound.

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QUANTITATIVE CHARACTERISTICS WHICH DETERMINE THE POSSIBILITY OF USING COMPLEX COMPOUNDS IN VOLUMETRIC ANALYSIS

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The accumulation of quantitative characteristics for the stability of complex compounds is of great importance for analytical chemistry, since the possibility of using a given complex compound in chemical analysis, is, in a number of cases, determined by the value of its instability constant. The most important lines along which the use of complex formation in volumetric analysis is being developed are the following.

1. Direct titration of solutions of metal addends with complexing agents and back titration (mercurimetric, and cyanometric titrations, titrations with complexones, etc.). The term "complexometric titration" proposed by Schwarzenbach for titration with complexones, should be extended to all these methods.

2. Masking side reactions by complexing the interfering element (e.g., iodometric determination of copper in the presence of iron (III) in which the latter is masked by using pyrophosphate, or fluoride, etc.).

3. Conversion of the test ion into a large complex cation, or anion, followed by precipitation of the large ion formed by an ion of opposite charge, (e.g., precipitation of the thiosulfate complex of cadmium with luteo-salt, or precipitation of the iodide complexes of cadmium with large cations).

4. Use of the formation of colored complexes for determination of equivalence points (e.g., the use of iron thiocyanate complexes for determination of trivalent iron by means of complexones, or titanometrically).

In complexometric titration the highest possible accuracy is determined by the value of the instability constant of the complex formed, and by the initial concentrations of the reactants. Developing the propositions advanced by us previously [1], we reckon that the accuracy of titration is determined by the ratio of the concentration of a given material at the equivalence point to its initial concentration. We denote the reciprocal logarithm of this ratio by pT, and call it the index of titration accuracy (for pT = 3, e.g., the accuracy of titration is $\pm$ 0.1%, for pT = 2, the accuracy may be $\pm$ 1%, etc.). From this it follows that:

$$pC = pC^0 + pT, \qquad (1)$$

where pC and pC^0 are the reciprocal logarithms of the concentrations of the given material at the equivalence point and at the beginning of titration, respectively.

In cases of reactions of the type

$$M + A = MA \qquad (I)$$

the following equation can be easily derived

$$pC^0 + 2pT = pK, \qquad (2)$$

where pC^0 is the reciprocal logarithm of the initial concentration of one of the materials, while pK is the reciprocal logarithm of the dissociation constant of compound MA (in the case of a complex – the reciprocal of the instability constant). Equation (2) is derived on the assumption that the initial concentrations of M and A are equal, while the changes in volume which occur during titration are negligible. This equation can be used both for evaluating the maximum achievable accuracy of a titration, and for evaluating the minimum values of pK and the initial concentrations, for any given accuracy of titration.

On titrating 0.1 M solutions to an accuracy of 0.1%, pK should be greater than 7 ($K_{inst.} \leq 10^{-7}$). We have shown previously [1], that when a complex of the type MA_n is formed, and 0.1 M solution is used, the addendum pK_n should obey the condition

$$pK_n > 4n + 3,$$

Comparatively few complex compounds obey this condition (the cyanide complexes of most metals, the thiosulfate complexes of silver and mercury, the ethylenediamine complexes of copper and nickel, the chloride, bromide, and iodide complexes of mercury, the phosphate complexes of iron, the complexes of bivalent and trivalent metals with ethylenediaminetetracetate, and some others).

The condition just formulated is an essential condition, but it is still insufficient in cases of complexes which dissociate step-wise. On titrating to a limiting saturated form, it is essential that the constant of the last stage should be less than 10^{-7}, while for titration to one of the intermediate stages, it is essential that this particular form should accumulate in solution to a sufficient extent (~99.9%).

If there are complexes of the type MA_1, MA_2, and MA_3 present in solution, then the relative amounts of the complex of type MA_2 can be expressed by the approximation:

$$\alpha = \frac{\kappa_2 C_A}{1 + \kappa_2 C_A + \kappa_2 \kappa_3 C_A^2}, \tag{3}$$

where κ_2 and κ_3 are the step-wise stability constants corresponding to complexes of type MA_2 and MA_3, while C_A is the equilibrium concentration of addendum A.

After differentiating this equation and equating the first differential to zero we get

$$C_A = \frac{1}{\sqrt{\kappa_2 \kappa_3}}. \tag{4}$$

Substituting this value of C_A in equation (3) gives for the maximum relative content of the given complex

$$\alpha_{max} = \frac{\sqrt{\kappa_2/\kappa_3}}{2 + \sqrt{\kappa_2/\kappa_3}} \tag{5}$$

or

$$\alpha_{max} = \frac{\sqrt{K_3/K_2}}{2 + \sqrt{K_3/K_2}}, \tag{5a}$$

where K_2 and K_3 are the step-wise instability constants of complexes of type MA_2 and MA_3.

From equation (5), it follows that the maximum accumulation of a given complex is determined by the ratio of the step-wise constants. Thus, the relative content of a given intermediate form can only exceed 98% for a ratio of the step-wise constants of more than 10^4.

If the addendum A is a base, then for certain pH values the dominant form will be particles of HA, and the equation for the reaction occurring during titration will be of the form:

$$M + HA = MA + H^+. \tag{II}$$

At the equivalence point the reciprocal logarithm of the concentration of M and HA are equal to $pC^0 + pT$, while the concentration of MA is practically the same as the initial concentration. The equilibrium constant of reaction (II) is equal to the ratio of the dissociation constant of HA to the instability constant of complex MA.

From which it follows that

$$pC^0 + 2pT = pK - pK_D + pH. \tag{6}$$

Equation (6) can be used for a number of calculations. As an example we adduce the calculation of the minimum values of pH at which a given titration can be carried out with a given accuracy. For an accuracy of $\pm$ 0.1% and an initial concentration of 0.1 M.

$$pH_{min} = pK_D - pK + 7. \tag{6a}$$

If the dominant form in the system is particles of H_2A, while the reaction proceeds with the formation of complex MA, and the freeing of two protons, then equation (6a) will be modified and assume the form:

$$pH_{min} = \tfrac{1}{2}(\Sigma pK_D - pK + 7), \tag{6b}$$

where ΣpK_D is the sum of the indices of the step-wise dissociation constants of particles H_2A. Equation (6) can also be used for other cases after minor modifications.

By means of such equations it is possible to calculate the minimum pH values (for titration accuracies of $\pm$ 0.1%) for titration reactions of ethylenediaminetetracetate with a number of cations. These values are given in Table 1.

TABLE 1

Minimum Values of the pH for Titration of Cations with Ethylenediaminetetracetate ($Edta^{4-}$) (pT = 3, C^0 = 0.1 M)

Cations	pK for the complex	Minimum value of the pH during titration
Mg^{2+}	8.7	9.3
Ca^{2+}	11.1	6.9
Mn^{2+}	13.5	4.9
Fe^{2+}	14.2	4.5
Hg^{2+}	15.7	3.8
Co^{2+}	16.1	3.5
Cd^{2+}	16.5	3.4
Zn^{2+}	16.7	3.3
Ni^{2+}	18.4	2.4
Cu^{2+}	18.4	2.4

In all cases where masking is involved, a definite reaction is implied, to which masking can be applied. Such reactions may be reactions involving complex-formation, precipitation, and oxidation-reduction. Here we shall consider masking in relation to complex-forming reactions; the same type of reasoning and the general conclusions drawn will also apply in other instances. On addition of a material B to a solution containing ions M, a complex of type MB_n is formed, and the reaction between this complex and addendum A will proceed according to the following equation:

$$MB_n + A = MA + nB. \qquad (III)$$

For practically complete masking (pT = 3) at the equivalence point, (the reciprocal logarithm of concentration A is not less than $pC^0 + 3$), the concentration of MB_n should be practically equal to the initial concentration, while the concentration of MA should not exceed 0.1% of the initial concentration ($-\log C_{MA} \geq pC^0 + 3$). Since the equilibrium constant of reaction (III) is equal to the ratio of the instability constants of complexes MB_n and MA, then the condition for masking can be formulated as follows:

$$pK_{MA} - pK_{MB_n} \leq pC^0 - npB. \qquad (7)$$

For masking in 0.1 M solution and for a molar concentration of the masking material (B):

$$pK_{MA} - pK_{MB_n} \leq 1. \qquad (7a)$$

In this case which often happens, practically complete masking can be achieved if the instability constants differ by less than an order of 1, or the instability constant of complex MB_n is less than the instability constant of complex MA. There is practically no masking, if at the equivalence point, the concentration of MA is practically equal to the initial concentration, while the concentration of MB_n is at least a few thousand times less than the initial concentration ($-\log C_{MB_n} \geq pC^0 + 3$); then:

$$pK_{MA} - pK_{MB_n} \geq pC - npB + 6. \qquad (8)$$

If the initial concentration is 0.1 M, while the concentration of addendum B is 1M, then

$$pK_{MA} - pK_{MB_n} \geq 7 \qquad (8a)$$

and consequently there will be no masking, if the instability constants differ by a factor of 7.

TABLE 2

pK of Certain Zinc Complexes

Complex	pK	Complex	pK
$ZnEdta^{2-}$	16.7	$Zn(P_2O_7)_2^{6-}$	6.5
$Zn(CN)_4^{2-}$	16.7	ZnHCitr	4.2
$Zn(OH)_4^{2-}$	16.0	ZnS_2O_3	2.2
$ZnEn_2^{2+}$	12.1	$ZnSO_4$	2.3
$ZnN(CH_2COO^-)_3$	10.3	$ZnCH_3COO^+$	1.6
$Zn(NH_3)_4^{2+}$	9.46	$ZnCl^+$	0.15
$Zn(C_2O_4)_2^{2-}$	7.38	$ZnBr^+$	−1.0

Table 2 lists the indices of the instability constants of several zinc complexes. The results adduced show that on titration of a zinc salt with ethylenediaminetetracetate, complete masking is only possible on addition of cyanide and excess alkali; masking will be incomplete when ethylenediamine, and nitriltriacetate are used, while ammonia, oxalate, pyrophosphate, citrate, thiosulfate, sulfate, acetate, and halides do not mask the reaction considered at all.

Equations (7) and (8) may be used to give a rapid assessment of the possibility of masking a particular reaction with various complexing agents, if data on the instability constants of the respective complexes are available.

Volumetric methods can be applied by complexing a given ion and then precipitating the complex ion formed with a large ion of opposite charge

$$M + nA = MA_n; \qquad (IV)$$

$$R + MA_n = RA_nM\downarrow. \qquad (V)$$

For titration to an accuracy of up to 0.1%, the concentration of a material M (as simple and complex ions) in the region of the equivalence point should be at least a thousand time less than the initial concentration

$$(C_M + C_{MA_n}) \leq 10^{-3} C^0 \quad (9)$$

In order that this condition can be observed it is essential, first and foremost, that the minimum value of the solubility product of the salt RMA_n

$$P_s < 10^{-3} C^0 C_R. \quad (10)$$

Since the concentration of R ions in solution may be made fairly high, then the solubility product of the given complex salt may also have comparatively high values (of the order of 10^{-6}–10^{-8} for initial concentrations of 0.1 M).

Completeness of precipitation also depends on the value of the instability constant of complex MA_n. The concentration of the complex ion can be found from the solubility product of RMA_n.

$$C_{MA_n} = \frac{P_s}{C_R}. \quad (11)$$

while the concentration of the free metal can be determined from the inequality (9) and equation (11). After substituting these values and simplifying, we get

$$\frac{10^{-3} C^0 C_R - P_s) C_A^n}{P_s} \geq K. \quad (12)$$

It follows from equation (12) that for this method of determination, it is possible to use comparatively unstable complexes (K can have large values), if P_s is small compared with $10^{-3} C^0 C_R$ and there is excess of free addendum in solution.

An indicator should change its color near the equivalence point, and at this point the concentration of test material (C_M) should be within certain concentration limits. C_M should here be at least a thousand times less than the initial concentration (the upper limit for a titration accuracy of ± 0.1%), and correspond to an excess of the second material, also not exceeding 0.1% of its initial concentration (lower concentration limit of M). In the simplest case [Reaction (I)], these conditions can be written as:

$$pC^0 + 3 \leq pM \leq pK - 3. \quad (13)$$

There are indicators which form colored soluble compounds and colored precipitates. Because the approach in both cases is similar, we have confined ourselves to a discussion of the first.

For the reaction:

$$M + I = MI, \quad (VI)$$

where I is the indicator, while MI is the colored compound, in accordance with the law of mass action we can write

$$pM + pI - pMI = pK_i. \quad (14)$$

In this equation pK_i is the index of the instability constant of complex MI.

Titration is usually carried out to a definite indicator color; consequently, the value of pMI characterizes the sensitivity of the indicator and is a constant for a given indicator. The value of pMI should be fairly large — the indicator should not combine with significant amounts of the titrated metal. Every indicator is characterized by a constant value (IC), determined by the indicator sensitivity, and by the index of the instability constant of the complex MI

$$IC = pK_i + pMI. \quad (15)$$

In order that a given reaction may be used for indicating, it is essential that its IC should be within definite limits, since the value of pM should be confined within a definite range (equation 13):

$$pC^0 + 3 + pI < IC < pK - 3 + pI. \quad (16)$$

As an example, let us consider the use made of the formation of FeCNS for the determination of the titration end point, during determination of ferric iron. In this case pK is 2.4 (2) while pFeCNS is ≈4. From this IC = 6.4. Normally the concentration of cyanide used is 0.01 M, from which

$$pC^0 + 5 < 6.4 < pK - 1. \quad (16a)$$

In this case, therefore, the initial iron concentration should be greater than 0.04 M, while the value of pK for the dissociation reaction of complex FeA should be greater than 7.4.

SUMMARY

1. The possibility of carrying out a direct titration in which a complex is formed in solution is determined by the value of the instability of the respective complex formed, by the initial concentration of reagents, and by the pH value. Equations are derived by means of which it is possible to calculate limiting values of these factors for a given accuracy of titration.

2. Completness of masking is determined by the ratio of the equilibrium constants of the masked and masking reactions, and also by reagent concentrations. The equations derived can be used for evaluating the completeness of masking in various cases.

3. The possibility of using complex formation followed by precipitation of the complex ions in volumetric analysis, is determined in the first instance by the value of the solubility product of the complex salt formed. In this case unstable complexes can also be used.

4. The conditions necessary for the application of colored complex compounds for determination of titration end points are considered.

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A VOLUMETRIC METHOD FOR THE DETERMINATION OF COBALT WITH DIMETHYLGLYOXIME

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Few methods are known for the volumetric determination of cobalt: a potentiometric titration based on oxidation of cobalt with potassium ferricyanide in ammoniacal media [1], precipitation of trivalent cobalt compounds with subsequent titration with a reducing agent [2], and titration with potassium cyanide [3]. It is often inconvenient to use these methods for a number of reasons, such as the necessity of using filtering and washing apparatus, and also (in the case of the last two groups of methods) because of difficulties connected with removal of nickel. The development of new volumetric methods for cobalt determination is, therefore, a matter of interest.

Cobalt gives a stable, soluble compound with dimethylglyoxime. The present article contains some data on the possibility of titrating cobalt with dimethylglyoxime in the presence of an external indicator, such as that suggested previously for nickel determination [4-6]. All the experiments which we carried out were made on mixtures of salt solutions; the cobalt content of the original solution was determined gravimetrically.

Titration of Cobalt with Dimethylglyoxime in Mixtures not Containing Nickel

Complex formation between the cobalt ion (II) and dimethylglyoxime occurs to some extent even in weakly acid media. The addition of alkali or ammonia favors full and rapid complexing of cobalt to give a soluble complex, in which 1 g atom of cobalt corresponds to 2 g molecules of dimethylglyoxime. As a result of this reaction, there is formed initially a bivalent cobalt compound of a dark brown color [10], this compound, however, is unstable in ammoniacal media and changes fairly rapidly to a trivalent cobalt derivative with the same ratio of its components. Oxidation is accompanied by a change from the brown color to a light yellow; this facilitates determination of the titration end point when an external indicator is used. A strip of filter paper soaked with an ammoniacal solution (ammonia + ammonium chloride) of a nickel salt and dried in an oven can serve as the external indicator. Cobalt forms a more stable compound with dimethylglyoxime than nickel, the dimethylglyoxime added to the solution, therefore, first of all combines with cobalt, when excess dimethylglyoxime is present, the indicator paper is colored red. The working solution was an alkali solution of dimethylglyoxime; 11.6 g of dimethylglyoxime recrystallized from water was dissolved in 200 ml of 1 N alkali and diluted to 1 liter. Its concentration was determined volumetrically by means of a standard nickel solution.

The conditions used for titrating cobalt in a solution of its pure salt were as follows. To a neutral solution of cobalt salt was added ca. 2 g of ammonium chloride and ammonia to form the cobalt-ammine. The solution obtained was diluted with water to 50-70 ml and titrated immediately. The first lot was titrated slowly with vigorous shaking of the containing flask, so that plenty of atmospheric oxygen is absorbed. To determine the end point, drops of the solution being titrated were now and again transferred with a glass rod to a strip of ordinary filter paper, attached to the indicator paper.* When a rose colored spot of nickel dimethylglyoxime appeared on the indicator paper, titration was stopped. The second lot of solution (the duplicate) was titrated rapidly. Having added almost the equivalent amount of reagent in one lot, oxidation of the dioxime of bivalent cobalt to the slightly colored complex of trivalent cobalt was affected either with atmospheric oxygen (shaking up the flask for 3 minutes) or with ammonium persulfate (0.1-0.2 g). When the solution had lightened it was titrated to the final end point. Ammonium persulfate cannot be added before starting titration, otherwise the cobalt will be oxidized before it has a chance to react with the dimethylglyoxime. The ammine of trivalent cobalt reacts slowly with dimethylglyoxime as a result of which very low results may be obtained. For the same reason, the ammoniacal solution of the cobalt salt to be titrated should not be kept long in the air. Table 1 contains the results of these experiments (Column 3 contains the means of two determinations).

* Sometimes, a brown precipitate of Co(II) dimethylglyoxime is formed in addition to the soluble reaction products; the precipitate can interfere with determination of the end point, if the test drop from the solution being titrated is placed directly on the indicator paper.

TABLE 1

Titration of Cobalt with Dimethylglyoxime in Solutions of Pure Cobalt Salts

Expt. No.	Cobalt taken (g)	Number of ml of 0.08925 M dimethylglyoxime	Cobalt found (g)	Error (relative) (%)
1	0.0059	2.32	0.0061	+3.4
2	0.0119	4.65	0.0122	+2.5
3	0.0178	6.95	0.0183	+2.8
4	0.0233	9.04	0.0238	+2.1
5	0.0297	11.47	0.0302	+1.7
6	0.0356	13.78	0.0360	+1.1
7	0.0418	15.74	0.0414	−0.5
8	0.0475	18.20	0.0479	+0.8
9	0.0534	20.38	0.0536	+0.4
10	0.0668	25.51	0.0671	+0.5
11	0.0751	28.85	0.0759	+1.1
12	0.0890	34.10	0.0897	+0.8

The results given in Table 1 show that if 0.04–0.09 g of cobalt is taken, then for a final volume of the titrated solution of 100 ml, the relative error of titration is on average 1%. The results are usually on the high side.

The following experiments were carried out in order to establish the possibility of a direct titration of cobalt with dimethylglyoxime in mixtures, containing iron, chromium, aluminum, tungsten, molybdenum, and vanadium. In making up synthetic mixtures (in solution) corresponding in composition to cobalt alloys, we were guided by published results [7]. The following compounds were used: $CoSO_4$, $NiSO_4$, $FeCl_3$, $KCr(SO_4)_2$, $KAl(SO_4)_2$, $(NH_4)_2MoO_4$, $(NH_4)_2WO_4$, NH_4VO_3.

The conditions used for determination of cobalt in complex mixtures were fundamentally similar to those used for the determination of cobalt in pure cobalt salts. The difference was that ions of trivalent metals – iron, chromium, and aluminum – which give hydroxides in ammoniacal media were kept in solution by means of sodium pyrophosphate. The solution of cobalt salt plus respective amounts of the compounds listed above of the other elements was acidified with 10 ml of concentrated hydrochloric acid, 15 g of sodium pyrophosphate (as the crystalline hydrate) was then added and the whole heated to 70–80°. After cooling, concentrated ammonia was added to a permanent ammonia odor. Titration was carried out as described already. Pyrophosphate was not added to solutions containing molybdenum, vanadium, and tungsten but free from the trivalent metals. For high tungsten contents, in addition to ammonia, alkali was added in sufficient amount to dissolve the precipitate of tungstic acid.

Chromium, aluminum, and also the ions formed by sexivalent molybdenum and tungsten, and quinquevalent vanadium do not interfere with the titration of cobalt with dimethylglyoxime. The conditions employed above fail only when determining cobalt in the presence of iron. Despite the fact that only trivalent iron was used in preparing the synthetic mixtures, the solution being titrated was often colored raspberry, the color which is characteristic of the dimethylglyoxime complex of bivalent iron. This can be explained on the grounds that, in ammoniacal solution, particularly in the presence of extraneous complexing agents, the value of the oxidation potential Co^{3+}/Co^{2+} is strongly reduced, as a consequence of which the reduction of trivalent to bivalent iron by complex ions of bivalent cobalt becomes possible. The higher the ammonia concentration, the easier iron is reduced. For low ammonia concentrations, this phenomenon is not observed. The red color of the solution, which is determined by formation of the dimethylglyoxime of bivalent iron, disappears on the addition of a few crystals of ammonium persulfate. Thus, when titrating cobalt in solutions containing iron, it is essential to avoid a large excess of ammonia. When, therefore, the titrated solution acquires a raspberry color, or a raspberry colored spot is formed on the indicator paper, which rapidly disappears on standing in the air, a little ammonium persulfate should be added to the solution.

The mean error (the sum of the absolute errors divided by the number of tests) amounts to 0.8%. The mean deviation from the true value (difference between the total amount of cobalt taken and the total amount found, relative to the amount taken) is positive and amounts to + 0.3% (Table 2).

Determination of Cobalt in Materials Containing Nickel (Indirect Method)

Direct titration of cobalt with dimethylglyoxime is impossible when nickel is present. Nevertheless on the one hand it is possible to titrate total nickel and cobalt in ammoniacal solution, while on the other hand, fairly simple conditions have been found, whereby nickel alone can be titrated without removal of cobalt. The amount of cobalt can accordingly be determined by difference. If the difference between the amount of cobalt and nickel is not very large, both metals can be determined together by the given method.

Direct Titration of Nickel with Dimethylglyoxime in the Presence of Cobalt

An explanation of how it is possible to titrate nickel with dimethylglyoxime in the presence of cobalt is of interest it itself. It has been shown previously [4–6], that nickel can be titrated directly with dimethylglyoxime in

TABLE 2

Titration of Cobalt with Dimethylglyoxime in Complex Salt Mixture

Expt. No.	Composition of mixture corresponding in composition to the following materials (%)	Cobalt taken (g)	Cobalt found (g)	Error (relative) (%)
1	Cobalt steel: Co-36; Fe-59.5; Cr-3.5	0.0589	0.0583	−0.7
2	Vikkaloy: Co-52; Fe-35; V-13	0.0589	0.0593	+0.7
3	Komol: Co-12; Fe-72; Mo-17	0.0637	0.0631	−0.9
4	Stellit: Co-41; W-25; Fe-3; Cr-26	0.0730	0.0737	+0.9
5	Vidia-1: Co-13; W-82; Fe-0.4	0.0601	0.0595	−1.0
6	Vidia 2: Co-6.1; Cr-87.4	0.0631	0.0637	+0.9
7	Sedit: Co-45; Cr-33; W-16	0.0730	0.0740	+1.1
8	Stellit: Co-50; Fe-0.5; Cr-20	0.0618	0.0620	+0.4
9	Tselsit: Co-31; W-25; Cr-26	0.0647	0.0654	+0.8
10	VK-6: Co-6; W-88; Fe-to 1	0.0671	0.0674	+0.4
11	VK-8: Co-8; W-84; Fe-to 1	0.0671	0.0666	−0.8
12	VK-15: Co-15; W-78; Fe-1	0.0642	0.0649	+1.1

steels and alloys free from cobalt. The method described then has not hitherto been applied to alloys which also contain cobalt.

A mixture of nickel and cobalt salts reacts differently with dimethylglyoxime according to the ratio of these metals and to the acidity of the medium. Thus, when equal amounts of the components react with dimethylglyoxime in a weakly acid medium, it is the nickel which reacts first. When a considerable part of the nickel has been precipitated, the next lot of dimethylglyoxime starts to react with the cobalt ions. In ammoniacal media, the reverse is true, i.e., the cobalt is the first to react. If there is more cobalt than nickel, then, independently of the acidity of the medium, some of the cobalt is complexed first and this is followed by complexing of some of the nickel. The reaction is totally different in ammoniacal solution, when the salts of nickel and cobalt are titrated with dimethylglyoxime, and the cobalt has been first subjected to the action of any oxidizing agent. In this case, even for a very large amount of cobalt, the dimethylglyoxime added first of all complexes almost all the nickel, and only after this stage, does it react with cobalt. This is precisely what happens during the qualitative and quantitative gravimetric determination of small amounts of nickel in materials rich in cobalt [8, 9]. We tried to take advantage of this sequence of reactions with dimethylglyoxime after oxidation of the cobalt, for the successive titration of nickel and cobalt. A mixture of cobalt and nickel salts to which has been added ammonia plus an ammonium salt was oxidized. After oxidation of bivalent to trivalent cobalt, the nickel was first titrated in solution with dimethylglyoxime using dimethylglyoxime paper as external indicator; cobalt was then titrated, a nickel indicator paper being used instead of the dimethylglyoxime indicator paper. Tests showed that in individual cases nickel can be actually titrated with a reasonable degree of accuracy, but subsequent determination of cobalt in the same solution was not feasible. Whichever oxidizing agent was used (hydrogen peroxide, ammonium persulfate and potassium ferricyanide were tried) and whatever the temperature at which oxidation was carried out, the ammine complex of trivalent cobalt formed as the result of the oxidation reacted so slowly with the dimethylglyoxime, that titration of cobalt was practically impossible.

The most reliable course proved to be titration of nickel in solution after oxidation of cobalt in ammoniacal media with ammonium persulfate to the purpureo salt $[Co(NH_3)_5Cl]Cl_2$.* This compound reacts much slower with dimethylglyoxime than the other trivalent cobalt ammines. Moreover, being fairly sparingly soluble in water (0.4%) in the presence of large chloride ion concentration, this compound can be almost completely precipitated. The solid purpureo salt in a saturated solution of ammonium chloride hardly reacts at all with dimethylglyoxime at ordinary temperatures. In order to convert cobalt into the precipitate of $[Co(NH_3)_6]Cl_3$ as rapidly and completely as possible the following procedure was adopted. To 25-30 ml of a neutral solution containing nickel and cobalt, was added 10-12 g of dry ammonium chloride and 7-8 ml of concentrated ammonia. To the solution of the ammines thus obtained was added 1-1.5 g of ammonium persulfate. Oxidation of the cobalt was first of all carried out at room temperature, the contents of the beaker being stirred until the precipitate of purpureo salt was formed. For very low concentration of cobalt, no precipitate of purpureo salt may form; this, however, will not interfere with subsequent conduct of the analysis. After 10 minutes, oxidation of cobalt was completed by heating. To destroy excess oxidizing agent, the mixture was boiled for 2-3 minutes. The solution was then cooled, and excess ammonia neutralized with hydrochloric acid until there was only a weak ammonia odor, diluted to 50-70 ml with water, and

* Apparently, other sparingly soluble ammine complexes of trivalent cobalt are formed as well as this basic oxidation product.

nickel titrated without filtering the precipitate of the purpureo salt. The end point was determined by means of dimethylglyoxime paper. Correct results were obtained, when, after oxidation of the cobalt, the solution above the precipitate was rose colored or a light yellow. When a yellow-brown solution was titrated (which indicates incomplete complexing of cobalt to $[Co(NH_3)_5Cl]Cl_2$) the amount of dimethylglyoxime used for titration was considerably higher, since in this instance, glyoxime also reacts with the cobalt. High results were also obtained on titrating in hot solutions, or in solutions with a high ammonia concentration.

Results on the determination of nickel in the presence of cobalt by the method just described are given in Table 3. The ratio of cobalt and nickel in the salt mixtures used was similar to the ratio of these metals in heat resistance and magnetic steels.

TABLE 3

Direct Titration of Nickel with Dimethylglyoxime in Solution after Conversion of Cobalt into $[Co(NH_3)_5Cl]Cl_2$

Expt. No.	Amount taken (g)		Ratio Ni:Co	Nickel found (g)	Error (relative) (%)
	nickel	cobalt			
1	0.0587	0.2348	1: 4	0.0585	−0.4
2	0.0657	0.7358	1:12	0.0667	+1.5
3	0.0681	0.0908	3: 4	0.0690	+1.3
4	0.0710	0.6390	1: 9	0.0720	+1.4
5	0.0599	0.0299	2: 1	0.0608	+1.5
6	0.0575	0.1150	1: 2	0.0578	+0.8
7	0.0593	0.0099	6: 1	0.0593	0
8	0.0704	0.0176	4: 1	0.0707	+0.4
9	0.0558	0.0490	1.3: 1	0.0563	+0.9
10	0.0481	0.0812	1: 1.7	0.0487	+1.2
11	0.0634	0.1278	1: 2	0.0642	+1.2
12	0.0640	0.1280	1: 2	0.0647	+1.2

The mean error was 1%, while the mean deviation from the true value was + 0.9%.

The effect of other metal ions such as iron, chromium, aluminum, molybdenum, tungsten, and vanadium which often accompany nickel and cobalt in their alloys was studied next. Sodium pyrophosphate (or pyrophosphoric acid) was used to mask the metal hydroxides in ammoniacal media, as before. In other respects preparation of the solution did not differ from that described above. It turned out, however, that the pyrophosphate ion hinders complexing of cobalt to $[Co(NH_3)_5Cl]Cl_2$, so that subsequent titration of nickel was unsatisfactory. In another variant, trivalent metals were precipitated with sodium fluoride. Cobalt was oxidized as usual without filtering off the fluorides. Nevertheless, even in these cases, although the oxidation of cobalt went in the required direction, reproducible results were not obtained. Positive results were only obtained after removal of iron, chromium, and the other metals by precipitation with zinc oxide (see below).

Titration of Total Cobalt Plus Nickel with Dimethylglyoxime

Total cobalt and nickel were precipitated under the same condition as for cobalt titration. The indicator was "nickel" paper. If there is more nickel than cobalt, then the end point can also be determined by means of "dimethylglyoxime" paper—disappearance of the red spot of nickel dimethylglyoxime. Ions of zinc, sexivalent molybdenum and tungsten, and quinquevalent vanadium do not interfere with titration of total nickel plus cobalt. Iron, chromium, and aluminum must be complexed to give soluble complexes, preferably pyrophosphates. From what has been said, it follows that total cobalt and nickel can be determined on separate aliquots without separation of many metals. The latter technique, however, is not essential, in so far as in practice, it is much more convenient to determine nickel and then total nickel and cobalt on one aliquot after removal of a number of interfering elements by zinc oxide.

Determination of Nickel and Cobalt in Solution after Removal of Iron, Chromium and Other Metals with Zinc Oxide

To an acid solution of mixtures 1, 2, 3, 4 and 5 (for their composition, see Table 4) was added concentrated ammonia till the hydroxides started to separate out. The precipitate was dissolved in a few drops of hydrochloric acid 1:1, after which 10-12 g of zinc sulfate (as the crystalline hydrate) was added. The idea was to lower the pH slightly to dissolve the zinc oxide and at the same time decrease loss of cobalt and nickel by coprecipitation with

TABLE 4

Volumetric Determination of Nickel and Cobalt with Dimethylglyoxime after Removal of Iron, Chromium and Other Metals with Zinc Oxide

Expt. No.	Mixture, composition of which corresponds to the following alloys (%)	Amount taken (g)		Amount found (g)		Error (relative) (%)		Suggested aliquot
		Co	Ni	Co	Ni	for Co	for Ni	
1	Heat resistant steel: Co-65; Ni-2; Cr-27; Mo-5	0.3804	0.0144	0.3856	0.0140	−1.3	−2.8	0.8
2	Heat resistant steel: Co-45; Ni-32; Cr-23; Mo-5	0.4848	0.3864	0.4866	0.3800	+0.4	−1.7	1.0
3	Heat resistant steel:* Co-45; Ni-4-5; Cr-20; Mo-20	0.4296	0.0480	0.4278	0.0480	−0.4	0	1.0
4	Heat resistant steel:* Co-42; Ni-20; W-4; Cr-20; Mo-4; Fe-4	0.4560	0.2280	0.4584	0.2258	+0.5	−1.9	1.0
5	Yakrit: Co-33; Ni-10; Mo-4; Cr-10; W-16	0.4380	0.1440	0.4290	0.1428	−2	−0.9	1.2
6	Magnetic alloy: Co-41; Ni-24; Cu-35	0.4200	0.2400	0.4140	0.2376	−1.4	−1.0	1.0

* Niobium is a component of these two alloys; it was not included in the synthetic mixtures.

the hydroxides of the metals being removed. The solution was then diluted to 150-170 ml, heated, and zinc oxide added till the Al, Cr, Fe were precipitated. The cooled mixture was transferred to a 250 ml standard flask, the mixture was filtered into the flask through a dry filter. Total cobalt and nickel was then determined on two 50 ml aliquots of the filtrate as follows. 5-6 g of ammonium chloride and 4-5 ml of concentrated ammonia was added to each aliquot before titration and then titration carried out as described above. Nickel was determined on two other aliquots from the same filtrate. In this case to each aliquot was added 15 g ammonium chloride and 7-8 ml of concentrated ammonia; cobalt was oxidized as described above. The mixture corresponding to alloy Number 6 was analyzed as follows. Copper was removed with aluminum turnings at the lowest possible acidity, without heating. The filtrate was transferred to a 250 ml flask. For total cobalt and nickel determination the procedure adopted was as follows. The aluminum which had dissolved in getting rid of copper was complexed with alkali tartrate. The procedure employed subsequently was the same as before. Preparation of solutions for nickel determination was carried out as if no aluminum were present. The amount of cobalt is equivalent to the difference in the titrant used for titrating total nickel and cobalt and for titrating nickel alone. Results of determinations are given in Table 4.

The errors for determining nickel and cobalt in solution after removal of interfering elements with zinc oxide is not greater than the error involved in titrating nickel and cobalt in solutions of their pure salts.

SUMMARY

1. A method has been developed for direct titration of cobalt with dimethylglyoxime in ammoniacal medium using as external indicator paper soaked with a nickel salt. Zinc, sexivalent tungsten and molybdenum, and quinquevalent vanadium, do not interfere with the titration, neither do trivalent iron, chromium, and aluminum in the presence of sodium pyrophosphate.

2. Conditions have been found under which nickel can be titrated directly with dimethylglyoxime in the presence of cobalt, after the latter has been converted into $[Co(NH_3)_5Cl]Cl_2$.

3. A method is described for the determination of cobalt and nickel when present together in solution, after removal of iron, chromium, and other metals with zinc oxide.

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THE SOLUBILITY PRODUCTS OF THE RUBEANATES OF COPPER, NICKEL, AND COBALT

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Rubeanic acid of the diamide of dithiooxalic acid $H_2NSCCSNH_2$, was synthesized and described by Liebig and Wöhler as long ago as the beginning of the last century [1, 2]. Vöickel [3], established its exact chemical formula in 1941; its structural formula, however, was not studied till much later by Wallach and a number of other research workers [4, 5, 6].

Rubeanic acid is obtained by the action of cyanogen on hydrogen sulfide; there are several methods for synthesizing it. Wohler, e.g., prepared rubeanic acid by passing cyanogen and hydrogen sulfide into alcohol. Wollner's method [7] consists in passing dry cyanogen gas into an alcoholic solution of $Na_2S \cdot 9H_2O$. On acidifying the solution with hydrochloric acid, rubeanic acid is precipitated as a red brown precipitate. There are also other methods for preparing rubeanic acid [8].

Rubeanic acid dissolves readily in alcohol, particularly on warming. On cooling an alcohol solution, bright red, needle-like crystals separate out. In the dry state, as in alcoholic solution, rubeanic acid is very stable. It does not dissolve in water, while on addition of water to an alcoholic solution of it, slight hydrolysis with separation of sulfur occurs. On heating with strong potassium hydroxide, rubeanic acid is broken down with formation of KCNS, KCN and KHS. Strong acids break down rubeanic acid even in the cold, while weak acids break it down on heating; here the products are H_2S, S, and oxalic acid. Ammonia does not react with rubeanic acid so that it can be used as a solvent.

Wallach (1891), drew attention to the fact that the acidic properties which rubeanic acid exhibits in solution do not correspond to the accepted structure, and suggested the existence of two forms.

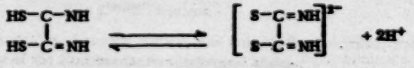
Thioamide

and

Isothioimide

P. Ray and R. Ray [9, 10], showed that in solution, rubeanic acid is in equilibrium with its acidimido form:

In this instance, the diimide form behaves as a weak acid:



(I) (II)

Addition of alkali to a solution of it shifts the equilibrium toward the acid-form (II), while in the presence of acids, the equilibrium is displaced to the left (I). As a result, the ratio of these forms depends on pH. Experiment shows that this fact is of vital importance in many reactions with rubeanic acid.

Rubeanic acid did not find practical application for a long time, although it was known that it forms stable compounds with the heavy metals Pb, Ag, etc. [..2]. After the work of P. Ray and R. Ray, Baudish, Feigl, Wübbing, and Steiger [11-18], it was established that rubeanic acid forms very stable compounds with many heavy metals. These compounds which have been called rubeanates, are inner complex compounds consisting of two five-membered rings with a general formula:

The high sensitivity of the reaction with rubeanic acid has been used in micro analysis for the determination of copper, nickel, cobalt, platinum, palladium, and other elements [10, 12, 13, 17].

Rubeanic acid is a specific reagent for those chemical elements which occupy the middle of the long periods in Mendeleev's Table, and for certain elements on their left [17].

Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge
Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn
W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb

By using the different reactions of chemical elements to rubeanic acid in the presence of organic complexing agents, we succeeded in separating the heavy metals into groups suitable for the needs of polarographic analysis [19]. During a study of metal complexes with rubeanic acid, we established that the rubeanates of iron, lead, and bismuth and other elements are less stable than the tartrates, oxalates, citrates and other compounds, and accordingly are not formed in the presence of the latter. On the other hand, copper, nickel, cobalt, zinc and cadmium readily react with rubeanic acid, even in the presence of a considerable excess of citrates, and are precipitated as slightly soluble compounds.

It is possible accordingly, to separate small amounts of copper, nickel, cobalt, zinc, and cadmium from considerable excess of iron, aluminum, manganese, and other accompanying elements, very simply and with great accuracy.

For a complete separation of small amounts of nickel, cobalt, copper, zinc, and cadmium by means of rubeanic acid, it was necessary to establish the optimum conditions for effecting this process.

Determination of the Solubility Products of the Rubeanates of Copper, Nickel and Cobalt

The solubility product (P_s) rule derived by V. Nernst (1889)* has been subjected to some essential modifications in the last twenty years. Thus, it has been established that the law of mass action, on the basis of which P_s is derived, is inapplicable to the case of strong electrolytes, and that "inert" electrolytes have a considerable effect on the value of the solubility product.

An explanation of these facts, and a solution of the problem of solubility is to be found in the latest achievements of thermodynamics in the study of ionic strength in solution, and on activities, etc.

At infinite dilution, activity and ordinary concentrations are equivalent. It follows that the solubility product in a dilute solution (for t and p = const), is a constant (Kapustinsky [20]). Accordingly in the case of slightly soluble precipitates, the solubility product will satisfy the classical Nernst formula:

$$P_s = C^{+} \cdot C^{-} = \text{const.} \qquad (1)$$

We used this fact in studying the rubeanates of copper, nickel, and cobalt, the low solubilities of which enable the Nernst law to be applied without any of the limiting factors indicated above.

Solubility and Solubility Products of the Rubeanates of Copper, Nickel and Cobalt at 18°

Test rubeanate	Solubility in moles/liter				P_s of the rubeanates in pure water
	in pure H_2O	in 0.01 M NH_4OH	in 0.001 M HCl	in 0.1 M NH_4Cl + 0.1 M citric acid + 0.001 M NaOH + 0.001 M p...	
Copper	$5.8 \cdot 10^{-8}$	$7.7 \cdot 10^{-7}$	$3.0 \cdot 10^{-7}$	$6.8 \cdot 10^{-8}$	$7.67 \cdot 10^{-35}$
Nickel	$7.2 \cdot 10^{-8}$	$7.8 \cdot 10^{-7}$	$1.1 \cdot 10^{-6}$	$7.8 \cdot 10^{-8}$	$1.1 \cdot 10^{-35}$
Cobalt	$7.4 \cdot 10^{-8}$	$9.0 \cdot 10^{-7}$	$6.7 \cdot 10^{-7}$	$5.4 \cdot 10^{-8}$	$1.2 \cdot 10^{-35}$

* The product of the ionic concentrations in a saturated solution at constant temperature is a constant $C_+^n \cdot C^{m-} = P_s$ = const.

The very serious difficulties which crop up during determination of small amounts of copper, nickel, and cobalt for finding the solubility products of the rubeanates, were easily overcome by adopting a polarographic technique which is being successfully applied at present for solubility studies (I. V. Tananaev and Mizetskaya [21], et. al.).

In dealing with a study of the solubility products of the rubeanates, our main idea was to determine the conditions under which the rubeanates are least soluble. To solve this problem we tried the method of saturated solutions – shaking up the precipitate with solvent for a long time. The solubilities found for the rubeanates in pure water, in the presence of acid, alkali, etc. were used to form our final conclusions.

Calculation of the solubility products of the rubeanates in pure water were made according to the formula:

$$[Me^{2+}] \cdot [pK^{2-}] = P_s, \qquad (2)$$

where Me^{2+} is the ionic concentration, respectively, of copper, nickel, and cobalt in moles/liter of solution, while pK^{2-} is the concentration of rubeanic acid ions.

Mean values of all the results obtained are given in the Table.

These results show that the solubility of the rubeanates of copper, nickel and cobalt under equal conditions are almost the same. The lower solubility of copper rubeanate in 0.001 M hydrochloric acid ($3.0 \cdot 10^{-7}$ mole/liter, as against $1.1 \cdot 10^{-6}$ mole/liter for nickel, etc.) is an exception. This observation is in agreement with a property of copper established previously, viz., that it gives rubeanates in acid media; this is only known for certain noble metals (Pt, Pd).

It is evident from the Table that the solubility of the rubeanates of copper, nickel, and cobalt in ammoniacal media (in 0.001 M NH_4OH) is ten times higher than in pure water (pH 7). Formation of nickel and cobalt rubeanates is only possible in alkaline media. Substitution of ammonia by a weak solution of NaOH or KOH favors more complete separation of the rubeanates, which confirms their considerably lower solubility under the respective conditions.

The optimum conditions thus found for the separation of the rubeanates of copper, nickel, and cobalt can be maintained, even when the solution contains salts, e.g., a considerable excess of sodium citrate and ammonia, the presence of which, or the addition of which is essential for the experimental technique we have developed. The negligible solubility of the rubeanates under these conditions, of the order of $1.0 \cdot 10^{-7}$ mole/liter (see Column 5 in the Table), confirms our conclusions, and permits us to recommend a method for the separation of small amounts of copper, nickel, cobalt and cadmium, and other elements.

The slightly higher solubility of the copper, nickel, and cobalt rubeanates in ammoniacal media already noted, shows up the mistaken conclusions of a number of authors who talk about "limiting sensitivity" of reactions with rubeanic acid, when determinations of sensitivity were made mainly in the presence of ammonia (P. Ray, 1930; F. Feigl, 1930; and S. A. Voznesensky, 1939). The sensitivity of the reaction for copper, nickel, and cobalt with rubeanic acid which is accordingly decreased 10 times, is a result of the strong tendency of those elements to form amminez.

Rubeanic acid can, therefore, be used in analytical chemistry for purifying reagents, and also for preparing spectrographically pure salts for technical purposes.

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HIGH FREQUENCY TITRATION

II. CHANGES IN THE ELECTRICAL CHARACTERISTICS OF SOLUTIONS DURING TITRATION

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On the basis of the analogy between the curves obtained during high frequency and ordinary conductometric titrations, respectively [1], we established, in our previous paper [2], that changes in total resistance ΔZ of a cell are determined, primarily, by changes in active (ohmic) resistance ΔR, and not in capacity resistance ΔX_{C_1} of the solution. This question is considered in somewhat greater detail in the present article.

On applying a high frequency (H.F.) voltage to the outer electrodes of a cell, a current will flow through any aqueous electrolyte solution, the density of which I_{total} will be equal to the sum of the densities of the conduction and displacement currents, respectively [3, 4].

$$I_{total} = \chi E + \frac{\epsilon}{4\pi \cdot 9 \cdot 10^{11}} \cdot \frac{\delta E}{\delta t} = \chi E_0 e^{i\omega t} + \frac{i\omega E_0}{4\pi \cdot 9 \cdot 10^{11}} e^{i\omega t},$$

where χ is the specific electrical conductivity of the solution in $ohm^{-1}\ cm^{-1}$; E, the field potential in $volt\ cm^{-1}$; E_0, the voltage amplitude; ω the frequency in angular units ($\omega = 2\pi f$, where f is the frequency in cycles); and ϵ is the dielectric permeability.

For aqueous solutions of electrolytes, I_{total} is basically determined by ionic conduction, and, to a much lesser extent by the displacement of permanent or induced dipoles [5].

The specific electrical conductivity of aqueous solutions of electrolytes χ depends to a large extent on electrolyte concentration; with increase in the latter, χ as a rule, attains a maximum and then drops [6]; its value is determined by the nature of the electrolyte within certain limits.

The dielectric permeability of aqueous solutions of electrolytes, ϵ differs very little from ϵ for pure water (81); changes in ϵ with concentration and nature of the electrolyte are insignificant.

Thus, according to Dmitriev's results [5], ϵ for a 0.38% aqueous solution of NaCl measured at a frequency of ~300 Mc, , is equal to 78.5. Fradkina [7], investigating aqueous solutions of NaCl, KCl, $MgSO_4$, $CuSO_4$, $K_3Fe(CN)_6$, $K_4Fe(CN)_6$ in a concentration range up to 0.4 N, and in a frequency range of ~300–3,000 Mc, found that ϵ for the solutions is greater than ϵ for water, nevertheless, the absolute increase in ϵ is not more than 15–20 units.

Thus, changes in concentration and nature of the electrolyte during H.F. titration affect the active resistance R, and consequently the total conduction current, and have little effect on displacement current, which is proportional, according to the formula adduced above, to the dielectric permeability, ϵ.

In order to make a quantitative evalnation of changes in dielectric permeability of electrolyte solutions during titration, we used a set-up built on the lines described by Hall [14].

A cell of the condenser type was connected in the anode circuit of a H.F. generator – a 6E5 tube, into the grid circuit of which was connected a quartz crystal operating at a frequency of 2 Mc to stabilize the vibrations. Capacity changes in the solution during titration are compensated by means of tuned condensers; by changing the capacity of these tuned condensers, oscillation starts; this is shown by closing of the magic eye, or by changes in the grid voltage measured by a cathode voltmeter. This set-up permits recording of differences in capacity by connecting the cell to the terminals of fixed condensers differing from each other by tenths of a picofarad.

Nevertheless, on connecting a cell with HCl solutions of various concentrations (0.1–0.001 N) and titrating with NaOH in this set up, we could get no observable changes in capacity; and we were unable to determine equivalence points; the capacity changes which occur with changes in solution composition were apparently very small (< 0.1 picofarad).

Using a 36 Mc generator described below, we took curves relating current strength to concentration for trichloroacetic acid CCl_3COOH in two solvents: 1) in benzene (Curve 1); and 2) in water (Curve 2), Fig. 1. In both

instances, 0.1, 0.2 ... 1, 2, 3 ml of acid was added to 20 ml of solvent; the direct component of the H.F. current flowing through the cell filled with these solutions, was measured by means of the set-up described below. For benzene, changes in current strength were extremely small; on addition of 4 ml of acid the change in current was only 10 μA. For water on the other hand, addition of only 0.1 ml of acid led to a considerable change in current (>100 μA), on further addition of acid, the current reached a limiting value of ~115 μA.

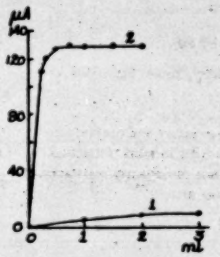


Fig. 1. Current changes through a H.F. cell. 1) Trichloroacetic acid added to 20 ml of benzene; 2) trichloroacetic acid added to 20 ml of water.

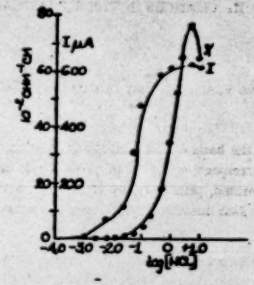


Fig. 2. Specific electrical conductivity (χ) and current strength (I) for various HCl concentrations.

In the first instance we were recording the displacement current, since in benzene (ε = 2.3), trichloroacetic acid is undissociated and exists as molecules in solution; in the second case, we were dealing with a conduction current which was determined by ionization of acid in aqueous solution.

The conductivity of aqueous solutions of electrolytes increases at very high frequencies, as a result of relaxation effects [8, 9]; all the same for the frequencies used in H.F. titration, this increase is insignificant. At a frequency of ~300 Mc, the increase in conductivity for a solution of 0.001 M $MaSO_4$, is not more than 4% greater than its low frequency value [7]; for 0.001 N H_2SO_4 solution in the frequency range 300-3,000 Mc, this increase amounts to ~8%, etc.. We can, accordingly, use the low frequency value [11], instead of the high frequency conductivity of aqueous solutions of electrolytes, without introducing large errors.

Fig. 2 shows a curve illustrating changes in H.F. current (in μA) with HCl concentration in aqueous solution, which we took with a set-up described previously [2]. The same figure also contains a curve for changes in χ, the low frequency specific electrical conductivity, for aqueous solutions of HCl at the same concentrations.*

Curve 1, current HCl concentration (c), to a certain extent is a repetition of the curve (χ - c). In dilute HCl solutions, current changes are insignificant; they have maximum values at average concentrations, then fall a little, and finally show a tendency to increase in concentrated solutions.

Comparison of the curves in Figs. 1 and 2, confirms our conclusions regarding the relation between change in current during H.F. titration and the active resistance or electrical conductivity of the solution, which according to the results given above, does not differ from the low frequency electrical conductivity in practice.

It follows that for solutions of electrolytes, the physical basis of H.F. titration and of the ordinary conductometric method, respectively, is identical; viz., changes in active resistance of the solution as a result of changes in ionic concentration during the formation of slightly dissociated reaction products, complex compounds, etc..

It should be noted, however, that the mechanisms whereby the direct (or low frequency) and H.F. currents, respectively, pass through solutions, containing emulsions, colloids, or fine crystalline suspensions, are different.

When a low frequency current is used in conductometric analysis, the suspension of fine crystalline precipitate formed during a reaction screens the field between the electrodes, as result of which titration curves are distorted. These distortions can be considerable if the precipitate separating out should cover the electrodes with a non-conducting

* The specific electrical conductivity was calculated from tabulated results for the equivalent electrical conductivity λ_c by means of the formula $\chi = \frac{\lambda_c c}{1000}$, where concentration is expressed in gram equivalents per liter [10].

or badly conducting layer, since, in such a case, the so-called cell constant l/S (where l is the interelectrode distance, and S is their area) changes. When a H.F. A.C. current, however is applied to a cell containing a solution in which there is a fine crystalline suspension or a fatty emulsion, this screening should decrease, or disappear altogether.

Actually, the capacity resistance x_c, offered by each suspended, non-conducting particle to the H.F. current, will fall according to the formula $x_c = \frac{1}{\omega c}$; where ω is the frequency, and c is the capacity of a suspended particle.

Similarily, precipitates formed on the inner cell walls as a result of a reaction will not hinder the passage of a H.F. current through a solution, and changes in the latter will correspond to concentration changes which result when such a reaction is used for titration purposes.

This effect, in our opinion, makes it possible to carry out H.F. titration in solutions of colloids, in suspensions, and in emulsions.*

Approximate ideas of the optimum frequency, and the sensitivity limitations of H.F. set-ups for titration can be gained as a result of mathematical analysis of the total resistance of a cell, z, made up from the equivalent scheme [2].

It should be noted that the application, by certain authors, of this scheme to cells with outer electrodes of any shape is incorrect. Strictly speaking, the equivalent scheme, depicted in our previous article [2], related to a cell with plane-parallel electrodes; for any other arrangement of the electrodes, the electric field inside the cell is extremely complex and cannot be described by a simple scheme.

It was shown above, that the dielectric constant of aqueous solutions is practically constant during titration; consequently, in the expression for z, not only c_2 (the capacity of the cell walls) but c_1 (the capacity of the solution) is also constant. By assuming that c_2 and c_1 are constant, it is easy to derive the following conclusions.

1) For a strongly conducting solution, the total cell resistance $z = \frac{1}{\omega c_2}$ is a constant; the current is determined by the constant (for ω = constant) resistance of the cell walls, and does not change (or changes by only an insignificant amount) for concentration changes during titration. Qualitatively, this conclusion is confirmed by the upper part of the current-HCl concentration curve, given in Fig. 2.

2) For dilute solution, (large values of R) the total cell resistance $z = \frac{1}{\omega} \cdot \frac{c_2 + c_1}{c_2 \cdot c_1}$ is a reactive resistance made up of two capacities in series, that of the cell walls and of the solution, respectively; the current changes to an insignificant extent during titration in dilute solutions; a H.F. set-up will have a low sensitivity (lower part of curve I-c, Fig. 2).

3) At low frequencies, ($\omega \to 0$), the capacity component of the total resistance, which is determined by the cell walls, has a high value, changes in the resistance of the solution are insignificant in comparison with the capacity component; the current hardly changes at all during titration.

4) At very high frequencies ($\omega \to \infty$), the capacity component of the solution becomes insignificant, and since it (because c_1 is practically constant) remains constant, the change in active resistance does not affect the current; consequently, even in this case a H.F. set-up is not sensitive to concentration changes.

From what has been said above, it follows that, in the first instance, in choosing the operating frequency, one should provide for a fairly large decrease in the reactive resistance of the cell walls so as to increase the relative changes in the actual resistance of the solution, and second, that the sensitivity of any H.F. set-up should be a maximum for certain mean concentrations of electrolyte.

EXPERIMENTAL

It was shown [2], that by increasing the frequency from 4 to 40 Mc one could use a beaker instead of a measuring tube for titration, i.e., the sensitivity of a set-up can be increased in accordance with the conclusions derived in the preceding section. A block scheme (Fig. 4), and a titration cell are described below, and results are given which are of interest to analytical chemists.

The cell, in contrast to the one described previously [2], is a glass beaker, the thickness of whose walls is 0,8 mm, while the internal diameter, and height are 21 and 73 mm, respectively (Fig. 3). The outer electrode rings

* Measurements of the concentrations of non-conducting solutions, e.g., in mixtures of organic polar and non-polar solvents, by means of changes in their dielectric permeability can be carried out with dielkometers,—apparatus for precision measurements of small capacity changes [13].

of brass 2, 3 (width 20 mm) are arranged on the lower part of the beaker at a distance of 1 mm from each other.

To decrease inductive and capacity effects, the beaker is mounted in a metallic screen 4. The H.F. current from the generator is led to the cell via a coaxial cable 5 through a socket, 7, fixed in the cell casing. The inner conductor of the coaxial socket, 7, is connected with the upper ring, 2; a diode DG-Ts8, 9, is connected between the lower ring, 3, and the inner conductor, 8, to rectify the H.F. current. The lower ring, 3, is also connected through a H.F. choke, 10, to the casing, and, consequently through the outer sheath of socket 7, and the screen of the coaxial cable to the generator chassis. The choke holds back the H.F. current and passes the D.C. current along the circuit-diode-microammeter.

An attenuator is necessary to regulate the H.F. voltage amplitude applied to the cell; this is a variable condenser with a capacity of 8-10 μF.

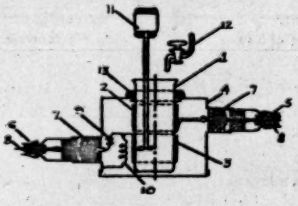


Fig. 3. Cell for H.F. titration. 1) Glass beaker; ϕ 21 mm, height 72 mm; 2,3) electrodes — sheaths of brass, width 20 mm; 4) metallic screen; 5,6) coaxial cables- 7) coaxial socket; 8) central conductor of the coaxial cable; 9) crystal diode DG-Ts8; 10) H.F. choke; 11) motor stirrer; 12) buret for titration; 13) supporting ring from plexiglass.

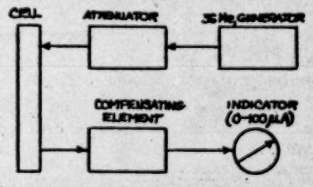


Fig. 4. Block scheme of set-up for H.F. titration using a 36 Mc generator.

On switching on the condenser its capacity increases and consequently the voltage applied to the cell increases, since the latter (together with the cable) acts purely as a capacitance load.

The 36 Mc generator was constructed as before [2], but with a few modifications. A loop consisting of an inductance L and a variable capacity C was introduced into the generator tube circuit, by means of which the generator and the cell and the microammeter connected to it are adjusted for maximum amplitude of the oscillations. Either a microammeter or a neon lamp can be used as an indicator in this set-up. Since current changes are very often small during titration, the sensitivity can be increased by means of the attenuator, by applying a greater voltage to the cell. In this case, the original current flowing through the cell is compensated by a reverse E.M.F., so that any original reading on the microammeter scale can be chosen, and subsequent readings during titration made up to a limit of 100 μA on the microammeter scale.

For this purpose a compensating battery with a constant voltage of 21.5 V is connected into the circuit, the voltage of the latter is regulated with a potentiometer, the crank of which is fixed on a panel. Titration is carried out at room temperature; the solution is stirred with a glass stirrer driven by a constant speed motor, 11.

In Fig. 5 curves are adduced which relate current flowing through the H.F. cell to concentration of HCl, NaOH, or NaCl. Both the arrangement of the curves, as well as their shape conform to the ideas developed above, regarding the mechanism whereby a H.F. current passes through an electrolyte solution.

1. Determination of Acid and Alkali in Aqueous-Alcohol Solutions of Synthetic Resins and Plasticizers, and Titration of Phenols*

Determination of the acidity of solutions of synthetic resins and plasticizers is of great importance for production control. A rapid determination of acidity in such solutions by means of colored indicators is not always possible, since the majority of these solutions have their own intrinsic dark colors.

* This investigation was carried out at the instigation of workers of the Scientific Research Institute of the Plastics Industry, and was carried out in conjunction with B. P. Ershov and V. L. Pokrovskaya. Work on the determination of free acid and alkali in solutions of plasticizer and synthetic resins, and on the determination of phenols, and other components, during production of synthetic resins will be continued with the cooperation of the above Institute.

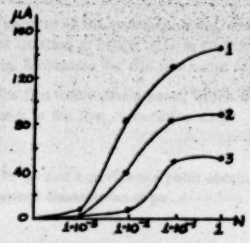


Fig. 5. Change of conductivity current with concentration: HCl (1); NaOH (2); and NaCl (3).

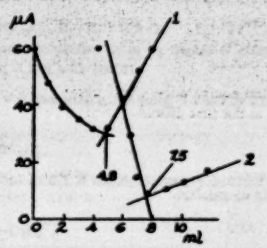
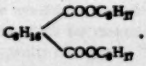


Fig. 6. H.F. titration of HCl with NaOH. 1) In a 10% alcoholic solution of phenol-formaldehyde resin; 2) in a 5% aqueous solution of "Epoxy" resin.

Potentiometric titration by means of platinum or glass electrodes, as well as conductometric analysis is also out of thequestion, since the electrodes are fouled during titration, and their normal operation interfered with.

We carried out experiments on titration of free HCl in an aqueous-alcohol medium of a 10% solution of phenol-formaldehyde resin — "Epoxy" (Fig. 6). In both cases, 10 ml of resin solution and 10 ml of water were poured into the titration beaker. In the first case (Curve I), 4.0 ml of 0.1 N NaOH was used to neutralize the HCl, while in the second, the volume of NaOH was 7.5 ml; these values correspond to free HCl contents of 0.017 and 0.27 g, respectively. These amounts differ by only 0.2% from the theoretical amounts.

Fig. 7 represents the titration curve obtained for 10 ml of a saponified solution of the plasticizer dioctylsebacinate,



to which 10 ml of water was added. In this case, excess alkali remaining after saponification was titrated with 0.5 N HCl. The equivalence point corresponded to an expenditure of 3 ml of 0.5 N HCl, which was equivalent to 0.087 g NaOH.

To determine phenol, excess alkali was added to the solution, and the volume of acid used for the sodium

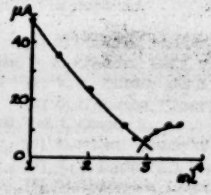


Fig. 7. H.F. titration of dioctylsebacinate

Fig. 8. H.F. titration curve of oxalic acid with 0.1 N NaOH.

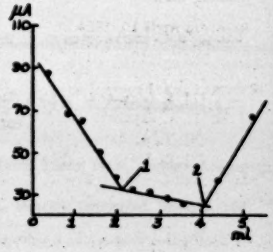


Fig. 9. H.F. titration of Na_2S with 0.1 N HCl.

phenolate, found by difference between the volumes for the final end point (V_2), and the initial point (V_1) corresponding to titration of free alkali.

These results, on titration of acid in the presence of diphenylpropane resin, demonstrate the possibility of this method, for solutions containing non-conducting particles and emulsions.

2. Titration of Dibasic Acids and Bases

The ratio of the two dissociation constants of oxalic acid $H_2C_2O_4$, $K_1 : K_2 = 6.5 \cdot 10^{-2} : 1.1 \cdot 10^{-5} \approx 6 \cdot 10^{+3}$ is too small for titration of oxalic acid to its first equivalence point, potentiometrically or by means of colored indicators [12]. Fig. 8 contains the titration curve for 5 ml of 0.1 N $H_2C_2O_4$ 0.1 N with NaOH.

The first equivalence point, which is clearly defined, and was obtained after using 2.5 ml of 0.1 N NaOH, corresponds to the first dissociation stage.

$$H_2C_2O_4 = H^+ + HC_2O_4^-.$$

The second equivalence point obtained after addition of 5 ml of 0.1 N NaOH, is poorly defined and corresponds to the second dissociation stage

$$HC_2O_4^- = H^+ + C_2O_4^{2-}.$$

The titration of Na_2S with 0.1 N HCl is illustrated in Fig. 9. In accordance with the two dissociation stages of H_2S ($K_1 = 3.31 \cdot 10^{-7}$, $K_2 = 2 \cdot 10^{-15}$), there are two equivalence points on the titration curve. The first corresponds to the formation of the hydrosulfide $Na_2S + HCl = NaHS + NaCl$, the second to the reaction $NaHS + HCl = NaCl + H_2S$. The amount of Na_2S in solution can be determined from the difference in the volumes corresponding to these two equivalence points; e.g., in this particular instance $2(4.08-2.10) = 3.96$ ml 0.1 N HCl, which corresponds to 0.015 g Na_2S.

Rough tests showed further that determination of Na_2S is possible, but to a lower degree of accuracy, when the solution also contains NaOH, the first equivalence point corresponding in this case to the total amount of HCl used to titrate NaOH, and to titrate Na_2S to the hydrosulfide.

We should like to thank G. I. Skanavi, N. N. Tunitsky, V. G. Vasilev, and I. P. Alimarin for their assistance.

SUMMARY

1. Results on the dispersion of the dielectric permeability of aqueous electrolyte solutions at high frequency, and analysis of the results of H.F. titration lead to the conclusion that this method has much in common with normal conductometric methods. In both methods, the effects which are measured during titration, are determined by changes in the ohmic resistance of the solution, and not by capacity changes.

2. By means of an electrical equivalent scheme for cell + solution, the sensitivity of the H.F. titration method is considered for limiting values of the resistance of the solution, and of the frequencies used.

3. A set-up including a 36 Mc generator has been developed for H.F. titration, and examples are given of its use for acid-alkali titration in aqueous-alcoholic solutions of synthetic resins and plasticizers, determination of phenols, etc..

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DETERMINATION OF CESIUM AS CESIUM BISMUTH IODIDE

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None of the chemical methods in use at present for the quantitative determination of cesium is accurate enough.

Although many good methods can be recommended for the analysis of individual cesium compounds, considerable difficulties crop up when attempts are made to determine this element in the presence of various contaminants, particularly rubidium and potassium.

Determination of cesium by means of antimony trichloride has been worked out to a greater extent than other methods. This method is based on a reaction first discovered by Godeffroy [1], who established that on addition of a concentrated solution of antimony trichloride in hydrochloric acid to a solution of cesium chloride, white crystals of a binary salt are precipitated.

The formula for this compound, $2SbCl_3 \cdot 3CsCl$, was established by Saunders [2].

Strecker and Diaz [3], on the basis of this reaction, worked out a method for determining cesium in the presence of rubidium, while Moser and Ritschel [4], increased the accuracy of the method considerably; even then, however, the method was still regarded as being not accurate enough, the results obtained were 4-5% lower than the true figures.

Later on, O'Leary and Papish [5] suggested silicotungstic acid for separation of cesium from rubidium. A number of methods for detecting and determining cesium is based on the characteristic property of this element to form ternary halogen salts with tin and the noble metals. For example, Vogel [6] suggested determining cesium as $Cs_2AgAuCl_6$.

All the same, the methods enumerated above and their variants are too complex and the reagents not too easily available considering the low accuracy they are capable of in the final count. As a result, a search for new and more convenient and accurate methods for the quantitative determination of cesium has not come to an end, and, as is evident from recent literature reviews [7, 8], some new ideas have been put forward which have not yet been checked in sufficient detail. One of the simplest, and most interesting methods for the determination of cesium is the method developed 20 years ago by N. A. Tananaev and Garmash [9], based on the precipitation reaction of cesium bismuth iodide discovered by Wells [10].

The authors of this method established that the precipitated salt had a constant composition $Cs_3Bi_2I_9$, and studied its properties.

According to their description, a hot solution of bismuth iodide in hydrogen iodide is poured into a saturated solution of the alkali salts with careful stirring; after leaving to cool, the solution is filtered off, and the precipitate washed with a saturated solution of the complex salt, and then with water at 7°.

The washed precipitate is dried for $1\frac{1}{2}$-$1\frac{3}{4}$ hours in a thermostat at 140-150°, and weighed as $Cs_3Bi_2I_9$. The authors checked the method on solutions of the alkali metals, containing 0.005-0.5 g of the iodide, chloride, and carbonate of cesium. 98.8-99.2% of cesium was precipitated in the presence of a considerable excess of other alkali elements, including a tenfold excess of rubidium. On an average, for the determination of cesium in admixture with other alkaline elements, 99.05% of cesium was precipitated. Feldman [11, 12], in checking this method, established that after precipitation of the complex salt, a certain amount of cesium chloride remains in solution, so that not more than 94% of the latter is precipitated; for a ratio of 1:4 of cesium to rubidium in solution, the analytical results are on the high side. Feldman also determined the solubility of $Cs_3Bi_2I_9$ in water, this was found to be 5% of the aliquot of cesium chloride taken for analysis. From these results, Feldman concluded that precipitation of cesium as $Cs_3Bi_2I_9$ has no advantages over other methods, and cannot be recommended for determination of cesium in minerals.

The observations of Perelman [13], are nearer the truth. He reckons that the method should be studied in greater detail, and conditions found whereby satisfactory results can be obtained, since precipitation of cesium as a complex salt has great advantages over other methods, from the point of view of availability of reagents and the extreme simplicity of the technique.

In the present article we give the results of a study devoted to a new check-up on this method, and indicate how it can be used for the analysis of pollucite, and of solutions which contain other alkali metals and the alkaline earth elements as well as cesium.

EXPERIMENTAL

In the first series of experiments, the determination of cesium as the double salt was carried out on aliquots of cesium chloride (Table 1); in this series we decided to reduce the volume from which cesium was precipitated.

TABLE 1

Test No.	Aliquot of CsCl (g)	Volume of solution (ml)	Volume of precipitant (ml)	Total volume (ml)	Weight of the double salt (g)	Cesium determined (%)
1	0.0657	1.0	8.5	9.5	0.2516	98.73
2	0.0657	1.0	8.5	9.5	0.2515	98.70
3	0.0657	1.0	8.5	9.5	0.2513	98.60
4	0.0657	1.0	8.5	9.5	0.2515	98.70
5	0.0657	1.0	4.7	5.7	0.2514	98.65
					Mean	98.68

The precipitant used was a solution of bismuth iodide in hydrogen iodide containing acetic acid. The test solution of cesium chloride was usually evaporated to dryness on a water bath, and then 1 ml of water added to the dry residue to dissolve it; precipitant was added to this in an amount greater than that required for complete precipitation.

Conditions for washing the precipitate of $Cs_3Bi_2I_9$ were studied at the same time. It was established that washing the precipitate with cold water leads to partial hydrolysis of the compound, and cannot be recommended. No better results were obtained by washing with 0.1 N hydrogen iodide, since the latter partially dissolves the precipitate.

On the basis of the work carried out on the properties of $Cs_3Bi_2I_9$ before, and cited above [9], it was found that the best results are obtained by washing the precipitate of the double salt with commercial 96%, or better still, glacial acetic acid; this was subsequently used in all cases.

The results given above show that the average percentage of cesium determined in its pure salts approximates to the value found by Tananaev and Garmash, and exceeds that found by Feldman.

Nevertheless, since the percentage of the cesium determined is still low compared with the amount actually present, and further improvements in precipitation by cutting down the volume of original solution of the test element is impossible, it was decided to carry out a second series of experiments on pure cesium salts (Table 2). In this series, cesium was determined on aliquots of 2.5 to 200 mg of cesium chloride.

TABLE 2

Test No.	Amount taken (g)	Volume of test solution (ml)	Volume of precipitant (ml)	Total volume (ml)	Weight of double salt (g)	Cesium determined (%)
1	0.0128	1.0	2.0	3.0	0.0499	100.00
2	0.0128	1.0	2.0	3.0	0.0496	99.50
3	0.0208	1.0	3.5	4.5	0.0808	99.58
4	0.0523	5.0	3.5	8.5	0.2017	99.47
5	0.0657	5.0	3.5	8.5	0.2549	100.00
6	0.0657	5.0	3.5	8.5	0.2554	100.20
7	0.0657	5.0	3.5	8.5	0.2548	99.99
8	0.1611	10.0	3.5	13.5	0.6259	100.20
9	0.1611	10.0	3.5	13.5	0.6219	99.54
10	0.1984	13.0	7.0	20.0	0.7658	99.54
11	0.1984	13.0	7.0	20.0	0.7654	99.51
12	0.1984	13.0	7.0	20.0	0.7670	99.72

The essential difference in this series, was that the dry cesium chloride was dissolved in the minimum amount of glacial acetic acid, and precipitation of cesium was effected by means of a solution of $KBiI_4$ in glacial acetic acid.

N. A. Tananaev's instructions in his first article [14] on the quantitative determination of cesium as $Cs_3Bi_2I_9$ were used as a guide for preparing the $KBiI_4$. According to Tananaev, the precipitant should be prepared as follows: to 1 g of Bi_2O_3 is added a saturated solution of 5 g KI in water. The mixture is shaken and heated to the boil. 25 ml of glacial acetic acid is then added in small amounts; on heating this solution a light orange colored solution of the precipitant is obtained.

We modified his procedure in that we excluded any water and managed to get a more concentrated solution. We proceeded as follows: 5 g of Bi_2O_3 is mixed dry with 17 g KI. To this mixture is added 50 ml of glacial acetic acid (or acid of a concentration not less than 95%), after which the mixture is heated to the boil with constant stirring. The mixture usually dissolves completely, and the precipitant solution is ready for use.

It is evident from Table 2, that in the absence of water in the test solution, and by using concentrated precipitant, it is possible to determine cesium in aliquots of its chloride with good accuracy, on amounts of 12-200 mg (10-150 mg, calculated as metal) of chloride.

Determination of cesium in amounts less than 10 mg requires the use of very small volumes, which are inconvenient for ordinary laboratory technique. Larger amounts (> 100 mg) necessitate increasing the volume before precipitation to 10-13 ml and increasing the volume of precipitant accordingly.

When, however, we come to analyzing solutions which also contain the alkali and alkaline-earth elements, as well as cesium, and not just solutions of pure cesium salts, the conditions for determining cesium must be modified, since not all the chlorides, and even fewer of the sulfates and other salts are soluble in acetic acid.

It was established that the chlorides of potassium, lithium, rubidium, magnesium, and iron dissolve relatively easily in acetic acid, and that the chlorides of ammonium, sodium, calcium, and aluminum are only slightly soluble. Accordingly, in the general case, for determination of cesium in a mixture of chlorides of the alkali and alkaline-earth elements, and also in the presence of aluminum chloride, it is necessary, first of all, to dissolve the dry residue in the minimum amount of water, and then to carry out precipitation of the double salt from a strong acetic acid medium. The following procedure can be recommended: the solution of chlorides containing cesium, is poured into a 25-40 ml beaker (depending on the estimated cesium content) and evaporated on a sand bath to dryness. The dry residue is then dissolved in the minimum amount of water, normally about 1 ml and not more than 3 ml for most of the accompanying chlorides, and finally acetic acid added, also in an amount depending on the estimated cesium content:

Cesium content, in mg (calculated as metal)	Amount of CH_3COOH to be added, in ml
10-40	2
40-80	5
80-120	10
120-160	12

The total concentration of the acetic acid solution thus prepared should not be less than 85%. The test solution is next heated, and a hot solution of precipitant added with careful stirring; precipitant is used at the following rate:

for 10- 40 mg cesium	add 2	mg precipitant	
" 40-120 " "	" 3.5	"	"
"120-140 " "	" 5	"	"
"140-180 " "	" 7	"	"

After addition of precipitant the beaker is covered with a clock glass and placed on a hot water bath for 1-1.5 hours to coagulate the crystals which separate out. The solution is then cooled, and filtered through a Number 4 crucible. The precipitate is washed with glacial acetic acid until the wash liquor is no longer colored yellow, this requires up to 25 ml of acid.

Washing should be carried out with small aliquots of acid. The washed precipitate is dried at 140-145° to constant weight; the conversion factor of $Cs_3Bi_2I_9$ to Cs_2O is 0.2159, while from CsCl to Cs_2O it is 0.8368.

Cesium can be determined in similar fashion from solutions of sulfates and carbonates. It is necessary to take into account the ratio of cesium to rubidium, since coprecipitation is appreciable for a ratio of these metals of 1:3. Accordingly, in the presence of appreciable amounts of rubidium, the total volume of acetic acid solution used for cesium determination should be doubled (2 ml of water and double the amount of acetic acid recommended above — the amount varying as before with the estimated cesium content).

Sodium, lithium, potassium, calcium, magnesium, aluminum and ammonium do not affect precipitation of cesium in acetic acid medium. The average percentage precipitation of cesium is 99.7.

This method can be used for analyzing various materials containing cesium, first and foremost, pollucite. It is best to open up the latter with hydrochloric acid. 0.20-0.40 g of the mineral, ground so as to pass a 100-120 mesh sieve, is treated in a porcelain crucible with 15 ml concentrated hydrochloric acid, and the contents of the crucible evaporated to dryness with frequent stirring. Treatment with hydrochloric acid is repeated twice more. The dry residue is lixiviated with hot water, and the solution filtered into a 100 ml beaker. The precipitate is finally washed on the filter with hot water to a negative reaction with sodium silicomolybdate.

The filtrate is evaporated to 5-8 ml and transferred to a 35-40 ml beaker, in which it is evaporated to dryness. 1 ml of ethyl alcohol (1:1) is added to the residue to dissolve it, followed by 5 ml of glacial acetic acid; cesium is then precipitated from the volume of solution thus obtained with precipitant solution.

Table 3 contains results of cesium determination on a sample of pollucite opened up by Tananaev's method, and by our technique. In the first instance, the mineral was opened with the usual mixture of hydrofluoric and sulfuric acids, as described in specialist textbooks [15, 16], while in the second instance, hydrochloric acid was used as recommended by us (Table 3). For comparison, the cesium content was determined in pollucite by the bromostannate method [17], the results found in this case were 26.21; 26.15; 26.34% Cs_2O.

TABLE 3

Weight of pollucite (g)	Volume before precipitation (ml)	Volume of precipitant (ml)	Total volume (ml)	Weight of double salt (g)	Cs_2O (%)
		By Tananaev's Method			
0.3027	10.0	25.0	35.0	0.3472	24.7
0.3088	10.0	25.0	35.0	0.3621	25.3
0.3157	10.0	25.0	35.0	0.3702	25.5
				Mean	25.16
		By the New Technique			
0.3693	5.0	3.5	8.5	0.4582	26.8
0.3486	5.0	3.5	8.5	0.4248	26.3
				Mean	26.55

SUMMARY

1. A method for determining cesium as cesium bismuth iodide has been investigated.

2. A new variant is proposed for preparing a concentrated solution ofprecipitant, so that by decreasing the initial volume of the test solution, total volume of the reactants is reduced to half of the amount used at present. The average percentage of cesium which can be precipitated from solutions of its salts is 99.75%.

3. A new procedure is outlined for the determination of cesium as cesium bismuth iodide, whereby cesium can be determined in solutions of its salts, which also contain sodium, potassium, lithium, calcium, aluminum, and rubidium (the latter for ratios of Cs:Rb of not more than 1:3).

The average percentage of cesium determined by this technique is 99.7%.

4. A new technique is recommended for opening pollucite for analysis, and the applicability of the bismuth iodide method to the determination of cesium in this mineral demonstrated.

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PHYSICO-CHEMICAL METHODS OF DETERMINING ANTIBIOTICS

II. THE ANTHRON METHOD FOR THE QUANTITATIVE DETERMINATION OF MANNOSIDOSTREPTOMYCIN

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Mannosidostreptomycin is streptomycin, to the N-methyl-l-glucosamine part of which a d-mannose group is linked. Mannosidostreptomycin and streptomycin are compounds with very similar physical and chemical properties. Nevertheless, the micro-biological activity of mannosidostreptomycin is approximately four times less than that of streptomycin, with respect to a number of test microbes. The amount of the mannosido-derivative in streptomycin preparations is accordingly, a very important characteristic, and its determination is of paramount importance.

A number of chemical methods for the determination of mannosidostreptomycin is based on the properties of its d-mannose group [1, 2, 3]; the most widely used of such methods is a colorimetric method, based on a reaction between the d-mannose group and a solution of anthron in concentrated sulfuric acid [2]. Anthron is a comparatively specific reagent for carbohydrates, and is widely used for their determination. We were, however, only interested in its use for free d-mannose, and the d-mannose group of mannosidostreptomycin.

We first tried the anthron method proposed by Kowald and McCormack [2]. According to their method, the reaction between an aqueous solution of d-mannose or of d-mannosidostreptomycin with anthron was carried out as follows: to an aqueous solution of d-mannose, stirred continuously by hand, was added a solution containing 0.2 g of anthron in 100 ml of 95% sulfuric acid. On adding the sulfuric acid to the water, the temperature rises considerably, and this helps on the reaction between the d-mannose group and anthron to give a characteristic green color. After spontaneous cooling of the solution to room temperature, the optical density of the solution is determined at λ = 6200 A. Water, to which anthron has been added, is used as reference standard.

We carried out all operations in conical flasks identical in shape and size, and with uniform thickness of their walls, so as to ensure constant heating and cooling conditions. Optical density was measured on a differential photoelectric colorimeter, using a filter with maximum transmission at λ = 6000 A. Cell length was 40 mm. All the same, we got considerable variations between our replicates on one and the same solution (Table 1).

TABLE 1

Reproducibility of Results Obtained using the Anthron Method Proposed by Kowald and McCormack
Solution of d-mannose, concentration 16 γ/ml

Test number	1	2	3	4	5	6	7	8	9	10
Optical density (λ = 6000 A)	0.463	0.475	0.470	0.435	0.469	0.450	0.495	0.452	0.468	0.460

The results in this table show a deviation of 13%.

Mechanical agitation with a glass stirrer operating at constant speed, and a standard time of addition of the anthron solution did not eliminate this scatter of results. We decided to determine the maximum temperature attained on mixing the solutions. A copper-constantan thermocouple, in which both wires were 0.08 mm in diameter was used for this purpose. The thermocouple was placed in a very fine glass sheath which was placed directly in the flask containing the test solution. The cold junction of the thermocouple was immersed in a snow-water mixture in a Dewar flask; a galvonometer was used to measure the E.M.F.

Thus, by carrying out a number of replicates on solutions of d-mannose and anthron preliminarily kept at a constant temperature, we found that, despite adhering to standard conditions, the maximum temperatures in individual experiments differed by 1-3°. We carried out a series of determinations, in which the d-mannose and anthron solutions were kept at different initial temperatures. These experiments showed that the optical density of the colored solution depends on a considerable extent on the initial temperature of the solutions to be added to each other.

Thus, for a solution of d-mannose with a concentration of 18 γ/ml, at an initial temperature of 15°, the mean optical density of 10 determinations, was 0.59, while for an initial temperature of 27°, the mean optical density was 0.45.

These tests convinced us that temperature has an important effect on the course of the reaction. Using the technique described above (viz., Kowald and McCormack's), it is practically impossible to get equal rises in temperature, and the same rate of cooling. In order, therefore, to get constant temperature conditions, it was necessary to change the reaction conditions between d-mannose and anthron. We cut down the concentration of sulfuric acid in the anthron reagent, since decreasing this concentration should lead to less heating of the solutions on adding acid to water.

We first prepared a solution containing 0.2 g of anthron in 100 ml 95% sulfuric acid, and then added to this 15 ml of water. Direct preparation of a solution of anthron in sulfuric acid diluted beforehand with water is unsatisfactory, because of the slow rate of solution of anthron in such a solution. The solution of anthron in sulfuric acid after dilution with water, was added to an aqueous solution of d-mannose or mannosidostreptomycin. The maximum temperature attained in this instance was 50-70 (according to the initial temperatures of the solutions), while the maximum temperature attained on addition of a solution in concentrated sulfuric acid was always above 100°.

After addition of the anthron reagent, diluted with water, the solution was immediately heated in a boiling water bath for 6 minutes, the time being checked with a stop watch. On heating, the green color deepens. After heating, the flask and solution were immediately immersed in water + ice. The optical density of the solution was then measured with respect to the optical density of the reference solution.

The 6 minute heating period was chosen as the result of tests on the relation between optical density of the final solution D and the duration of the heating period, τ. Curves of D against τ for initial solutions of d-mannose and a streptomycin preparation containing mannosidostreptomycin, respectively, are given in Fig. 1. The curves are similar, and the maximum is observed in both cases for a period of heating of 6 minutes. It is clear from Fig. 1 that changing the time for which the final solutions are kept at an elevated temperature may lead to increases or decreases in optical density. It follows that when the technique described above was used [2], it was to be expected that the optical density would decrease with high initial temperatures.

Fig. 1. Relation between optical density D of the colored solutions and duration of heating. o = d-mannose with a concentration of 26 γ/ml; Δ = solution of streptomycin mannosidostreptomycin with a concentration of the latter of 103 γ/ml.

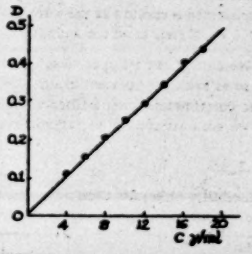

Fig. 2. Relation between d-mannose concentration c, and optical density D of the solution.

After studying the influence of anthron concentration on the optical density of the solution, we decided to use 0.1 g of anthron in 100 ml of concentrated sulfuric acid, since on decreasing the concentration further, a fall in optical density was observed, and at concentrations of anthron of 0.05 g anthron in 100 ml sulfuric acid, slight variations in the optical density was observed when the colored solutions were stood for 1 hour.

We showed that the maximum volume of water which will not lead to precipitation of anthron from a solution containing 0.1 g in 100 ml of concentrated sulfuric acid was 25 ml; in our subsequent experiments, however, we used 15 ml of water per 100 ml solution.

As a result of this preliminary work we developed the following technique for determination of mannosidostreptomycin.

METHOD

1. Preparation of anthron reagent. 0.1 g of recrystallized anthron is dissolved in 100 ml concentrated sulfuric acid. After the anthron has dissolved, 15 ml of water is slowly and carefully added. The anthron reagent thus

prepared is stood for 1 hour, after which it is ready for use. A fresh solution of anthron in sulfuric acid should be prepared daily.

2. Analytical procedure. To 7 ml of an aqueous solution of d-mannose or streptomycin preparation stirred continuously is added 23 ml of anthron reagent in a fine stream. Flask + solution are rapidly heated in the course of 6 minutes on a vigorously boiling water bath. Flask + solution are then rapidly cooled in crushed ice, and the optical density measured at room temperature on a differential photoelectric colorimeter, using a red filter. Optical density of the test solutions is measured with respect to that of a reference standard. A 40 mm cell is a convenient size to use. The green color of the solution is very stable, its optical density is practically constant for 4–5 hours.

The reference standard is 7 ml of water which is treated in exactly the same way as the test solution.

All analyses should be carried out in similar flasks, and if possible with equal thickness of their glass walls.

3. Construction of a calibration curve. We assumed that the optical density of solutions of the reaction products formed between equimolar solutions of d-mannose or mannosidostreptomycin, respectively, with anthron is the same. This assumption was borne out by the fact that the same results were obtained for the quantitative determination of mannosidostreptomycin by the anthron method, and by a physical method, based on repeated counter-flow partition of the streptomycin preparation [2].

d-Mannose (chemically pure) was used for constructing the calibration curve. The straight line characterizing the relation D-c, where c is the concentration of d-mannose in γ/ml, is shown in Fig. 2.

4. Calculation of the mannosidostreptomycin content. For determination of the concentration of mannosidostreptomycin in γ/ml, the concentration of d-mannose found from the optical density is multiplied by 4.13 (the ratio of the molecular weight of mannosidostreptomycin as the base, to that of mannose).

Table 2 contains the results of replicate analyses by this method.

TABLE 2

Reproducibility of Results for Analysis by the Anthron Method, when the Solution is Heated on a Water Bath
Solution of d-mannose, concentration 16 γ/ml

Determination number	1	2	3	4	5	6	7	8	9	10
Optical density (λ = 6000 A)	0.398	0.405	0.402	0.396	0.396	0.402	0.403	0.395	0.398	0.400

The greatest deviation is 3%, a reproducibility which is quite acceptable. A similar reproducibility is obtained for determination of mannosidostreptomycin in streptomycin preparations. By changing the temperature conditions for the reaction, therefore, we managed to improve the reproducibility considerably.

To carry out analysis, it is necessary to pay attention to the value of the optical density of the reference standard. This depends on the quality of the sulfuric acid and anthron. We used only chemically pure sulfuric acid, so that the optical density of the reference solution was not greater than 0.08. No explanation has been given yet as to what contaminants lead to an increase in the optical density of the reference standard.

Anthron was prepared in the laboratory by reduction of anthraquinone [4], and purified by a two-fold recrystallization.

SUMMARY

A new variant of the anthron method for determination of mannosidostreptomycin ensures a reproducibility of ± 1.5%.

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NEW COMPLEXONES

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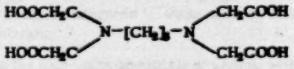
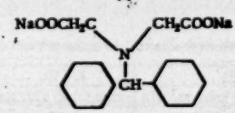
During recent years a number of papers have been published which have been devoted to the possibilities of using a new class of compounds in analytical chemistry; this class consists of compounds of α-aminopolycarboxylic acids and their derivatives, in which two or more acetic acid residues $-CH_2COOH$ are linked to nitrogen. Schwarzenbach [1] and coworkers, who studied their physico-chemical properties, and synthesized a number of them, called this class of compounds "Complexones". A characteristic feature of this class of compounds is their capacity to form very stable complexes which are soluble in water with most cations, particularly with the alkaline-earth elements, a feature which distinguishes them from other complexing agents known to date. The ones which have been most widely used are nitrilotriacetic acid, ethylenediaminetetracetic acid, and its disodium salt (Trilon B) and 1,2-diaminocyclohexanetetracetic acid, etc.. Papers have also been published which deal with the structure of the compounds formed between complexones and cations [2], and their application in various branches of chemistry [3].

Complexones can be used not only in analytical practice, but also for technological processes, e.g., separation or removal of valuable elements, etc..

During our studies we synthesized new complexones. Hexamethylenediaminetetracetic acid (I), and sodium benzhydrylaminediacetate (II), which have not been described in the literature, were prepared.



(I)



(II)

These compounds were synthesized by condensing sodium monochloroacetate with hexamethylenediamine, and benzhydrylamine, respectively, in an aqueous alkali medium.

Synthesis of Hexamethylenediaminetetracetic Acid

0.1 mole of hexamethylenediamine is dissolved in 37 ml of 25% sodium hydroxide, and 0.3 mole of monochloroacetic acid, neutralized beforehand with sodium carbonate, added to the solution. After heating for 6 hours at 50°, the reaction mass is acidified with hydrochloric acid till the solution is acid to Congo red, it is then evaporated.

Hexamethylenediaminetetracetic acid and a considerable amount of sodium chloride separate out. The latter is removed by washing the precipitate with ice water.

Hexamethylenediaminetetracetic acid is a white crystalline powder which is soluble in hot water and alkalies, slightly soluble in cold water, and insoluble in ethyl alcohol, acetone, benzene, and chloroform.

Analytical results are given below:

	Found %:	C 48.12;	48.10;	H 6.92;	7.05;	N 8.24; 8.28
$C_{14}H_{24}N_2O_8$.	Calculated %:	C 48.25;		H 6.8		N 8.05

Synthesis of Disodium Benzhydrylaminediacetate

0.1 mole of benzhydrylamine is mixed with 0.4 mole of monochloroacetic acid, preliminarily neutralized with 5 N sodium hydroxide. Condensation is carried out at 110° for 4 hours, an average pH of 8-10 being maintained by addition of a 5 N solution of sodium hydroxide. When the reaction is complete, the mixture is cooled. Disodium benzhydrylaminediacetate, which separates out, is recrystallized from 80% ethyl alcohol.

The preparation is a white crystalline powder, readily soluble in water, slightly soluble in alcohol, and insoluble in acetone, chloroform, dichloroethane, and benzene.

Found %: N 4.01; 4.12.

$C_{17}H_{15}O_4NNa_2$ Calculated %: N 4.08.

Polarographic Study of Hexamethylenediaminetetracetic Acid and Disodium Benzhydrylaminediacetate

In order to find out something about the complexing properties of hexamethylenediaminetetracetic acid and disodium benzhydrylaminediacetate, and in order to find out their possible uses in practice, both in chemical analysis and in polarography, these compounds were studied polarographically.

To establish the stability of the complexes formed, we chose the polarographic technique of determining shifts in the half-wave potentials of test cations in the presence of complexones. In all, 17 cations were tested. Tests were carried out in the presence of a series of buffer solutions.

Solution No. 1 (pH 2.5) – 0.4 M acetic acid; Solution 2 (pH 4.4) – 0.4 M acetic acid + 0.4 M sodium acetate; Solution No. 3 (pH 9.35) – 0.1 M ammonium hydroxide + 0.1 M ammonium chloride; Solution No. 4 (pH 12.4) – 0.1 M sodium hydroxide.

Test solutions were prepared as follows: 10 ml of a 0.01 M solution of the complexone (0.348 g $C_{14}H_{24}N_2O_8$ or 0.343 g $C_{17}H_{15}O_4NNa_2$ dissolved in 100 ml of water on heating), was measured into a 100 ml standard flask, and 3 ml of a solution of the test cation (1 mg/ml) and 1 ml of a 0.1% gelatin solution added, the whole being finally made to standard volume with one of the above mentioned buffer mixtures.

The cathode was a dropping mercury electrode fitted with a gadget to force the drops off the capillary, while the anode was a saturated calomel electrode. Polarograms were taken on a Heyrovsky type polarograph after hydrogen had been passed through the solution.

Tables 1 and 2 give the results for the half-wave potentials of cations with, and without complexones.

TABLE 1

Half-Wave Potentials of Various Cations in the Presence of Hexamethylenediaminetetracetic Acid

Test No.	Ion	pH 2.5		pH 4.4		pH 9.35		pH 12.4	
		without complexones	with complexones	without complexones	with complexones	without complexones	with complexones	without complexones	with complexones
1	Pb^{2+}	−0.38	−0.44	−0.43	−0.43	−0.18	−0.62	−0.70	−0.71
2	Cu^{2+}	+0.02	−0.12	−0.02	−0.14	−0.29	not reproducible	−0.05	−0.31
						−0.54			
3	Cd^{2+}	−0.60	−0.68	−0.62	−0.62	−0.62	−0.82	−	−0.88
4	Zn^{2+}	−1.08	−1.01	−1.09	−1.09	−1.28	−1.62	−1.52	−1.52
5	Ni^{2+}	−1.02	−1.03	−1.12	−1.12	−1.01	disappears	−1.37	−1.41
6	Co^{2+}	−1.22	disappears	−1.15	−1.21	−1.21		−1.37	−0.39
									−0.82
7	Al^{3+}	−	−	−	−	−	−	−1.29	−1.61
8	Bi^{3+}	−0.12	−0.12	−0.21	−0.21	turbid	−	−0.7	−0.7
9	As^{3+}	−1.02	−1.0	−	−	−	−	−	−
10	Mo^{VI}	−0.52	−0.52	−0.23	−0.62	−	−	−	−
				−0.62					
11	Mn^{2+}	−	−	−1.5	disappears	−1.64	−1.65	−	−
12	Cr^{3+}	−	−	−	−	−1.56	−1.73	−	−
13	Ti^{IV}	−0.65–0.97	−0.54	precip.	−1.02	−	−	−	−
14	Th^{IV}	−	−	−	−	−	−	−	−
15	Be^{2+}	−	−	−	−	−	−	−	−
16	La^{IV}	−0.62	−0.78	−0.72	−0.72	−0.68	−0.83	−	−
17	W^{VI}	−	−	−	−	−	−	−	−

It follows from the results adduced in Table 1 that addition of hexamethylenediaminetetracetic acid causes the half-wave potential to shift by varying amounts, as the differing stabilities of the compounds formed testify.

Lead forms a stable complex at a pH of 9.35, the half-wave potential of which is shifted by 0.44 V with respect to that of the simple ion.

Nickel forms such a stable complex at pH 9.35 that its wave disappears and no polarogram is obtained.

Cobalt forms stable complexes similar to that of nickel at pH's of 2.5 and 9.35.

Manganese forms a very stable complex at pH 4.4.

Copper and aluminum form complexes at pH 9.35 in which the half-wave potential has been shifted ~0.25 V.

Cadmium, zinc, and lanthanum form complexes at pH 9.35 in which the half-wave potentials have shifted ~0.2-0.3 V.

Bismuth, arsenic and molybdenum do not form complexes at a pH of 2.5-4.4; at higher pH's no polarograms were obtained under the test conditions.

Thorium, beryllium and tungsten are not reduced under the test conditions.

The results included in Table 2 show that addition of disodium benzhydrylaminediacetate also leads to formation of complexes of varying stability.

TABLE 2

Half-Wave Potentials of Various Cations in the Presence of Disodium Benzhydrylaminediacetate

Test No.	Ion	pH 2.5		pH 4.4		pH 9.35		pH 12.4	
		without complexone	with complexone	without complexone	with complexone	without complexone	with complexone	without complexone	with complexone
1	Pb^{2+}	−0.38	−0.42	−0.43	−0.42	−0.18	disappears	−0.7	−0.72
2	Cu^{2+}	+0.02	−	−0.02	+0.01	−0.29 −0.54	not reproducible	−0.05	disappears
3	Cd^{2+}	−0.60	−0.68	−0.62	−0.69	−0.62	−0.75	not reproducible	disappears
4	Zn^{2+}	−1.08	−1.01	−1.09	−1.05	−1.28	−1.19	−1.52	−1.47
5	Ni^{2+}	−1.02	−1.2	−1.12	−1.1	−1.14	−1	−1.37	disappears
6	Co^{2+}	−1.22	disappears	−1.15	−1.32	−1.21	−1.20	−1.37	disappears
7	Al^{3+}	−	−	−	−	−	−	−	−
8	Bi^{3+}	−0.12	−0.12	−0.21	−0.18	not reproducible	disappears	−0.7	−0.7
9	Mo^{VI}	−0.52	−0.52	−0.23 −0.62	−0.23	−	−	−	−
10	La^{IV}	−0.62	−0.62	−0.72	−1.1 −0.66	−0.68	−0.68	not reproducible	disappears

Lead forms such a stable complex at pH 9.35 that the wave disappears; lead cannot, therefore, be determined polarographically.

Copper forms a stable complex at pH 12.4 which is similar to that of lead.

Cadmium behaves like copper under the test conditions.

Nickel forms a very stable complex at pH 12.4, the waves of which disappear.

Cobalt forms complexes at pH 2.5 and 12.5, with stability similar to that indicated above.

Bismuth forms a stable complex at pH 9.35.

Lanthanum behaves like bismuth.

Zinc does not form complexes under the test conditions.

Aluminum is not reduced under the test conditions.

From these results it is clear that a number of cations form complexes, with the test complexones; on the results of these studies, therefore, it is possible to assess the applicability of these complexones for the polarographic deter-

mination of certain cations, and for masking interfering elements.

Study of hexamethylenediaminetetracetic acid and disodium benzhydrylaminediacetate as complexones in analytical and technological practice continues.

SUMMARY

1. Hexamethylenediaminetetracetic acid and disodium benzhydrylaminediacetate have been synthesized and characterized.

2. These compounds have been studied from the point of view of their use as complexing agents.

3. It has been established that they can be used in analytical practice, both for masking a number of elements, and for polarographic separation.

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LUMINOL INDICATOR PAPER FOR HYDROGEN PEROXIDE DETECTION

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Luminol (the hydrazide of 3-aminophthalic acid) gives a fairly bright chemiluminescence in the presence of small amounts of hydrogen peroxide; this phenomenon is only observed, however, when the pH of the medium is greater than 8 [1]. The brightness can be increased considerably by adding a catalyst such as potassium ferricyanide. The high sensitivity of this reaction for hydrogen peroxide has enabled biochemists to use it for detecting traces of hydrogen peroxide in biochemical materials [2].

Luminol paper is prepared either by soaking or spraying pieces of ashless filter paper with a 0.5% solution of luminol in 0.1 N sodium hydroxide; the papers are dried at 40° in an oven. Hydrogen peroxide is detected by placing a drop of test hydrogen peroxide solution and a drop of catalyst, e.g., a 1% solution of potassium ferricyanide, on a test paper. If hydrogen peroxide is present, then a bright chemiluminescence is observed. It was noticed, however, that with time, luminol paper prepared as described does not give such a bright spot as fresh reagent, though the original brightness could be brought back by addition of some more alkali. Reckoning, therefore, that the presence of alkali has a deleterious effect on the storage properties of the luminol paper, when preparing further lots of luminol test papers; we kept the strips for a few minutes, after putting the luminol on them, in a desiccator containing some formic acid, the latter counteracted the alkali of the test paper, and the strips were then dried as usual. When luminol paper prepared by this technique was then used for detection of hydrogen peroxide, the following procedure was adopted: first, the drop of test hydrogen peroxide was placed on the test strip, this was followed by a drop of catalyst, and a drop of alkali. The luminescence, which is very bright, can only be observed after adding the alkali.

Luminol paper prepared in this way, on storage for a year, under varying conditions, lost none of its sensitivity.

Sensitivity was determined by placing a drop of catalyst solution (a solution of 0.1 g of CuCl in 100 ml 1% ammonia) on a strip of luminol paper, and then adding a drop of dilute hydrogen peroxide, and observing development of any chemiluminescence. It was found that using such luminol paper, it is possible to detect hydrogen peroxide in 0.0005-30% solutions. Hydrogen peroxide in the concentration range 0.005-30%, gives a bright chemiluminescence when placed on a test paper. At a hydrogen peroxide concentration of 0.0005% the illumination is weak, but still clearly perceptible. Hydrogen peroxide can, therefore, be detected in a drop at a dilution of 1:200,000 by means of luminol paper.

Other materials, such as blood hemin and potassium ferricyanide can be used instead of the ammoniacal solution of copper as activators. In our tests, however, these other materials have no advantages over ammoniacal copper solution.

Instead of using luminol paper for detecting hydrogen peroxide, it can be used for detecting copper, by a spot technique as an ammoniacal solution, or for detecting potassium ferricyanide. Copper can be detected in one drop at a dilution of 1:100,000; while potassium ferricyanide can be detected at a dilution of 1:20,000. Similarly, a number of oxidizing agents can be detected, e.g., hypochlorous and hypobromous acids, their salts, and potassium permanganate. Chlorine and bromine can be detected in the gaseous form and also in aqueous solutions. In addition, various alkalis, gaseous ammonia, and other compounds can be detected. Since all these reactions can be carried out by spot techniques, while the basis of the method is the phenomenon of chemiluminescence, we are here dealing with a new technique of spot analysis, viz., chemiluminescent spot analysis, which takes its place alongside fluorescent spot analysis [3].

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CHRONICLE

VALERIAN LEVANOVICH KHUKHIYA

On October 17, 1954, after a short but serious illness, Valerian Levanovich Khukhiya died. He was an outstanding analytical chemist; who headed the Analytical Chemistry Laboratory of the Caucasian Institute of Mineral Raw Materials, a dean of the Chemical Faculty of the Stalin Tbilisi State University, a lecturer, and a Candidate of Chemical Sciences.

Khukhiya was born in 1904 in Khorsha. On finishing his course with honors (chemico-pharmaceutical and natural sciences) in Tbilisi State University, he remained there as an assistant in the Technical Sciences section. From 1933-1936 he was a lecturer in analytical chemistry. From 1936 he was head of the Analytical Chemistry Laboratory and lectured there.

In 1939 he successfully defended his thesis and got his degree of Candidate of Chemical Sciences.

From 1939, Khukhiya continued at the University, and at the same time became head of the Analytical Chemistry Laboratory of the Caucasian Institute of Mineral Raw Materials, where for five years, he developed research work; as a result of his untiring efforts an important research center on analytical chemistry has been created in Trans-Caucasia, and scientific personnel trained as analytical chemists.

During the last five years, the Analytical Chemistry Laboratory under his direction carried out over 20 research projects on important problems in the analysis of mineral raw materials, many of which have found practical application.

His scientific work was exceptionally varied and fruitful. He carried out about 60 pieces of research work, chiefly on analytical methods and on hydrochemical studies of mineral waters and useful deposits in Georgia.

Khukhiya was mainly interested in the hydrogeochemistry of the halogens (I, Br, Cl) in mineral waters in Georgia.

Working since 1933 on the study of various types of mineral water in Georgia, he noted a definite inter-relation between the coefficients of the ratios Cl/Br, Br/I (in certain cases Cl/I, also) and the type (group) of mineral waters. He used these indices later to explain the genetical chemistry of certain mineral waters.

He studied mineral waters in conjunction with the complex of factors which led to their formation. This was of special value as it made it possible to trace migration of I, Br, and Cl under complex conditions. His work along these lines was combined in a monograph "Hydrochemistry of Iodine, Bromine and Chlorine (Mineral Waters, in particular Water from Georgian Petroleum Deposits)", which was to be presented for his doctor's degree. Unfortunately, his premature and unexpected death did not allow him to carry out this idea.

Of special note are the practical results of his work devoted to the study and popularization of the well-known medicinal water "Lugela", and his work on improving "Borzhomi".

During the last war he organized the production of some chemicals vital to national defense.

The numerous young analytical chemists he has taught and trained are carrying out successful work in Scientific Research Institutes. He devoted a lot of his time and energy to social work. He was a member of the Praesidium of the Georgian Section of the Mendeleev All-Union Chemical Society for a number of years, and from its inception, was a member of the All-Union Society for the Dissemination of Scientific and Political Knowledge.

Both in his scientific work and in his personal relations, V. L. Khukhiya was always considerate, honest, a sympathetic comrade and a sincere friend.

The shining memory of Valerian Levanovich — as a objective, modest and hardworking scientist — will always live in the hearts of his pupils and comrades, and his image will serve as an example of sincere love and devotion to our great country.

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THE SECOND UKRAINIAN CONFERENCE ON CHEMICAL CONTROL IN THE METALLURGICAL AND METAL PROCESSING INDUSTRIES,

Convened to Celebrate the 300th Anniversary of the Union of the Ukraine with Russia,

And Held at Dnepropetrovsk from June 5-8, 1954

The second Ukrainian Conference on Chemical Control in the Metallurgical and Metal Processing Industries, convened to celebrate the 300th anniversary of the Union of the Ukraine with Russia, and called on the initiative of the Ukrainian Republic Branch of the D. I. Mendeleev All-Union Chemical Society in conjunction with the Dnepropetrovsk Section was held, with the active participation of workers from Institutes and factory laboratories.

219 representatives of 69 factories and various enterprises from 19 towns in the Ukrainian SSR were present at the conference.

The conference noted that Soviet analytical chemists have achieved significant successes in organizing the work of factory chemistry laboratories, and in the use of advanced physico-chemical and physical methods of production control.

New gravimetric, volumetric, colorimetric, and other methods, which have been widely applied, have been successfully developed by various Institutes, factories, and mining laboratories.

At the same time, the conference drew attention to a number of drawbacks; the following are the main ones:

1. Insufficient exchange of experience between advanced workers in factory laboratories.

2. Too little attention is paid to working out methods for determining small and trace amounts of elements and compounds.

3. Organization of spectrographic laboratories is far from satisfactory, as well as the training of personnel for spectrographic work, and specialists for gas analysis, chromatographic and other analytical methods.

4. Lack of ordinary apparatus; not enough analytical weights, insufficient measuring equipment (cylinders, standard flasks); production of even single beam photocolorimeters, galvanometers, and photoelements which find wide application in express analysis has not been organized. Not enough styloscopes, stylometers, and spectrographs are being turned out. The quality of spectrum excitation sources is not good enough.

5. The volume of scientific research work carried out in factory laboratories is far from adequate and does not satisfy essential industrial needs.

6. Standardization of technical analytical methods is in a very unsatisfactory state. The supply of standard samples is not good enough, particularly standards for spectrographic analysis of slags, fluxes, and individual elements. The output of essentially chemically pure reagents is too low.

7. There are not enough text books and monographs on photometric and electrochemical methods, and on gas analysis.

8. Cutting down the number of hours which students devote to analytical chemistry means that chemists are not well trained enough.

9. The standard of education and training of personnel, such as laboratory assistants and attendants is not high enough.

10. Little is done about comparing various analytical methods.

In order to solve the various problems which confront analytical chemists, the conference accepted the following resolutions.

Questions of Organization

1. To continue to strengthen the bonds between science and production, and to pay particular attention to publicizing the experience of inventors and the newest achievements of science and techniques.

2. To call Republic conferences at least once every two years. To call annual Regional conferences on individual analytical methods.

3. To increase the work of factory laboratories on periodic check-ups, corrections, and improvements in instruction and methods of production control.

4. To ask the Central Soviet of the D. I. Mendeleev All-Union Chemical Society to coordinate scientific research work on analytical chemistry, carried out by various Institutes and factory laboratories, and to give some attention to the production of filter papers (particularly ashless).

5. To pay more attention to developing physical and physico-chemical methods of gas analysis, micro- and semi-micro methods of qualitative and quantitative analysis, and to "in situ" analysis.

6. To increase research work on the theory of nephelometry, and colorimetry, the application of new organic reagents and photometric methods of analysis.

7. To carry out systematic work on the scientific study of new methods of breaking down ores, slags, and metals.

8. To pay particular attention to developing methods of determining small and trace amounts of elements and compounds; this is of great significance in the analysis of ores during production, of metals in the highest state of purity, and of analytical chemical reagents.

9. To carry out scientific research work in the fields of fluorescence analysis, spectrophotometric methods, investigation in the ultra-violet and infra-red, chromatography of inorganic materials, polarography and amperometric titration.

Personnel

10. That all branches of the All-Union Chemical Society should organize monthly refresher courses for workers in factory laboratories, on various methods of analysis, in the first instance on: 1) spectrographic analysis; 2) colorimetry; 3) gas analysis; 4) polarography.

11. To organize a 4-month course for increasing the qualifications of laboratory chiefs and their deputies, and to ask the Central Soviet of the All-Union Chemical Society to coordinate this with regard to arranging a program and suitable places to hold these courses, with the appropriate Ministries.

12. To ask the All-Union Chemical Society to expand and develop the training of personnel for chemical laboratories, to ask the Ministry of Ferrous Metals and of Agricultural Machinery Construction to support this request, and to develop it with regard to refresher courses for personnel, and to allot time for this work.

13. To ask the Central and Ukrainian Republic Soviet of the All-Union Chemical Society to issue the proceedings of the conference in a special publication "Communications on the Work of Members of the All-Union Chemical Society".

14. To ask the Ministry of Higher Education to improve the provision of laboratories and departments of analytical chemistry in State Universities, and to supply the modern apparatus necessary to train students in new methods of analysis and techniques.

15. To ask the Ukrainian Branch of the All-Union Chemical Society to request the Soviet of Ministers of the Ukrainian SSR and the USSR to organize in the Ukraine, taking the Konstantinov Glass Factory as a basis, the production of measuring cylinders, standard flasks, etc., and to set up an organization to provide Ukrainian factories with laboratory equipment.

16. To ask the Ukrainian Branch of the All-Union Chemical Society to call conferences of analytical chemists, not only on metals, but also in other fields (geology, fuel, the food industry) in which analytical chemistry is applied.

17. To draw the attention of organizations producing and supplying apparatus to the need of improving the quality and range of electrical apparatus and of electrical measuring apparatus for factory laboratories.

18. To ask the Ministry of Ferrous Metallurgy to organize, at one of the Institutes or factories in the Ukraine, a repair depot for laboratory equipment, as well as for improving equipment.

19. To ask the Ministry of Ferrous Metallurgy to review the working conditions in factory chemical laboratories and equalize payment to separate groups of chemists. To introduce a uniform bonus system.

20. To ask the Central Soviet of the All-Union Chemical Society to take upon itself the organization and issuing of catalogues indicating what apparatus is available and where from.

21. To put the question of supplying laboratory ashless filter paper and standardized micro weights to the Ministry of Ferrous Metallurgy.

22. To ask the Central Soviet of the All-Union Chemical Society to petition the Soviet of Ministers of the USSR regarding an increase in the supply and provision of reagents, apparatus, and equipment to factory chemical laboratories.

These resolutions were approved unanimously by all the delegates.

Chairman of the Analytical Chemistry Section
Yu. I. Usatenko

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